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A Survey of Atomic Constants (*).

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(*) Questa rassegna fu presentata dagli Autori al Convegno Internazionale sulle costanti fondamentali della Fisica, tenutosi a Torino, in onore di Amedeo Avogadro, nel Settembre 1956, e viene qui pubblicata in fascicolo a parte causa la sua mole e il suo carattere. Nei *Rendiconti* del Convegno — che usciranno tra breve in altro fascicolo del *Supplemento* — sarà di questa stessa rassegna dato un breve sunto. [*N. d. D.*].

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Nomenclature

Definitions of the principal symbols are given below. Other symbols are defined in the appropriate sections.

$\alpha = 2\pi e^2/hc$	Fine structure constant.
B	Magnetic induction (gauss).
c	Velocity of light (cm/s unless otherwise stated).
e	Electronic charge (esu).
e/c	Electronic charge (emu).
$F = Ne/c$	Faraday constant.
$\gamma_p = 4\pi\mu_p/h$	Gyromagnetic ratio of proton.
γ'_p	Apparent gyromagnetic ratio of proton in oil.
H	Magnetic field strength (oersted).
h	Planck's constant (erg s).
$\hbar = h/2\pi$	
k	Boltzmann constant.
λ	Wave-length (cm).
λ_g/λ_s	Conversion factor from Siegbahn scale to absolute units, i.e., 1 XU = (λ_g/λ_s) cm.
λ'	Wave-lengths in terms of Siegbahn scale, i.e., $\lambda' = \lambda_{cm}/(\lambda_g/\lambda_s)$.
M	Atomic or molecular mass (amu).
$M_p = Nm_p$	Atomic mass of proton.
m	Mass of electron (g).
m_p	Mass of proton (g).
μ_s	Magnetic moment of electron (emu).
$\mu_n = eh/4\pi m_p c$	Nuclear magneton (emu).
$\mu_0 = eh/4\pi mc$	Bohr magneton (emu).
μ_p	Magnetic moment of proton (emu).
μ'_p	Apparent magnetic moment of proton in oil.
N	Avogadro's number.
$\nu = \omega/2\pi$	Frequency (s^{-1}).
ν_c, ν_e, ν_n	See ω_c, ω_e, ω_n below.
ν_H	Hyperfine splitting of hydrogen.
$R = Nk$	Gas constant (erg/mole °C).
$R_\infty = 2\pi^2 me^4/ch^3$	Rydberg constant for infinite mass.
$R_H = R_\infty[m_p/(m_p+m)]$	Rydberg constant for hydrogen.
V	Voltage (volt).
$\omega_c = He/m_p c$	Cyclotron resonance frequency of proton (s^{-1}).
$\omega_e = He/mc$	Cyclotron resonance frequency of electron (s^{-1}).
$\omega_n = H\gamma_p$	Nuclear resonance frequency of proton (s^{-1}).

A) Object.

1. – Reasons for present study.

From time to time evaluations of the atomic constants have been made by various reviewers. Two of the most recent examples are those of DuMond and Cohen [1] and Bearden, Earle, Minkowski and Thomsen [2]. One area in which their results caused great concern was X-ray crystallography. In the past, X-ray wave-lengths were commonly expressed on the Siegbahn scale, i.e., in XU; one XU was approximately, but not exactly, one milli-angstrom (10^{-11} cm). After long consultation with the principal workers in this field a committee headed by Sir Lawrence Bragg [3] recommended 1.002 02 as the best value for the conversion factor from XU to absolute units, based on many direct measurements with ruled gratings by various investigators. This figure was thought to be correct to within .003 %. On the other hand, both the DuMond and Cohen and the BEMT [2] evaluations gave approximately 1.002 06.

This discrepancy has led to requests of one of the authors (J. A. B.) for a new direct determination of λ_g/λ_s. A preliminary study led to the conclusion that there were no new techniques available which would assure any major improvement in such a measurement and that it would be extremely difficult to obtain a significant increase in accuracy. At the same time a study was made of previous direct experimental determinations; no indications were found of any important systematic errors or of any uncertainties in the theory of ruled grating measurements as applied to X-rays. Thus the one remaining hope of resolving the dilemma seemed to lie in a new survey of the best values of the constants, which was therefore begun.

The λ_g/λ_s question is actually only one aspect of a problem raised by the two above-mentioned evaluations. In both cases it was found that the errors computed by external consistency were about 2.5 times those obtained by internal consistency. This can only mean that the accuracy of some or all experiments has been seriously overestimated. If this occurred more or less uniformly, no harm has been done, since the stated errors were based on external consistency. However, such a viewpoint is certainly an optimistic one. If the discrepancy is due primarily to a particular experiment or group of experiments, the results of the evaluations may be significantly in error. (Another aspect of the discrepancy concerns the best value of Avogadro's number N; this has been discussed at length in an exchange of letters between Straumanis [4] and DuMond and Cohen [5]).

A further reason for a new study of the constants is the experimental data reported since the DuMond and Cohen evaluation was completed in 1952. For example, there have been several determinations of the velocity of light, an X-ray experiment on calcite, and a measurement of the anomalous magnetic moment of the electron. While none of these results by itself implied any major change, together they seemed to warrant a new survey of the situation.

A final motive of the present report has been to attempt to summarize in one place the principal experiments which have been employed in calculating atomic constants. This should be of particular interest to textbook writers and physics teachers in showing just how the traditionally quoted measurements fit into the present picture.

2. – Previous evaluations.

In the early work in atomic physics there was a tendency to select one best experiment as fixing a particular constant or ratio. For example, Millikan's oil drop experiment was long regarded as giving the most reliable value of e. This approach gradually changed to a more critical review of all pertinent data. The *International Critical Tables* [6] contained a list of the principal physical constants compiled in 1923; a few years later an article by Henning and Jaeger in *Handbuch der Physik* [7] gave a more extended discussion of the subject. There was no adequate treatment of the errors in either case.

The most important single advance in the field came in 1929 when Birge [8] published a comprehensive evaluation of the physical constants with detailed discussion of the errors involved. In 1932 he made two additional contributions [9], an excellent summary of the theory of errors and a resurvey of the value of e, h, e/m, and α. The former provided the foundation for much of the subsequent work; it included discussions of the desirability of using probable error as a universal criterion, the distinction between internal and external consistency, and the use of the method of least squares. The latter had been previously employed by Bond [10] for simultaneous determination of e and h in a study of atomic constants. Birge's later work included a second comprehensive survey [11] published in 1942 and a new evaluation of e and N in 1945 [12], as well as numerous other contributions on more specialized topics.

Birge's method was usually one of successive approximation. He began with the most accurately known constants, which were independent or only slightly dependent on the others. After fixing these, he used them consistently in subsequent calculations and worked his way through the less precise data step by step to determine all the required constants. The least squares method was sometimes used to simultaneously evaluate two constants, but not as a generalized procedure. While the procedure of successive approximations is open to some theoretical objections, it worked well in practice and could be understood relatively easily. The same approach was also used in studies of atomic constants by von Friesen [13] and Stille [14].

A new step was taken by Dunnington [15] in 1939 by making several simultaneous least squares calculations of e, m, and h. His primary aim was to find the cause of the inconsistency of the data then available by omitting one questionable item in

each calculation. The generalized least square method was used in three studies by DuMond and Cohen [1, 16]; their chief purpose was to determine the best values of the constants, rather than search for discrepancies. The values given in the last report are now in general use. One of the major contributions of DuMond and Cohen was to emphasize the importance of correlations between the results of various experiments when the same factor contributes a significant part to the error of each one. If such correlations exist, it is necessary to eliminate them by reformulating the problem or to treat them by a special method developed by Cohen.

In 1951 Bearden and Watts [17] published an evaluation of the atomic constants, using the generalized least squares method. This work was continued by Bearden, Earle, Minkowski and Thomsen [2]. The results were presented only in condensed form, since they appeared almost simultaneously with the last DuMond and Cohen report and involved no significant differences in the values of the constants.

3. – General considerations.

There are at least four primary benefits of these evaluations: (1) Perhaps the most obvious one is to introduce a single set of values which can be used by all workers in the field until it becomes obsolete and is superseded by a new study. (2) A reviewer presumably can take sufficient time to study carefully all items in the literature which are likely to influence the best values of the constants. Even so, many reviews have omitted or misinterpreted some significant data; there is certainly no guarantee that the present study will be an exception. (3) A more subtle reason lies in the need for obtaining a self-consistent set of results. For example, a certain X-ray experiment performed several years ago gives h/e as the final result; but the value of c^2 is needed in the calculations leading to this. If one blindly uses such a figure for h/e together with a recent determination of c to obtain e/hc, it is equivalent to assuming two contradictory values of c in different parts of the calculation. On the other hand, a careful evaluation of a set of physical constants is unlikely to contain such obvious inconsistencies. (4) A study of the constants may point out certain discrepancies, which can lead to important new experimental and theoretical investigations.

Out of the various surveys the group referred to as the atomic constants has crystallized in relatively definite form. It is usually understood to include e, h, m, c, and N. Of these, c has sometimes been treated as a variable to be adjusted and sometimes as an auxiliary constant, whose value is known with much greater accuracy than the others. The same has held for the Faraday constant $F = Ne$. In recent years, as a result of the possible correlation of errors pointed out by DuMond and Cohen [1], it has also become necessary to include among the atomic constants λ_g/λ_s, the conversion factor between absolute wavelengths and X-ray wave-lengths measured on the Siegbahn scale. This factor hardly belongs to the group in its own right, but must be treated

with them as long as X-ray experiments play an important part in the results. Hence the group may now be said to include six constants: e, h, m, c, N, and λ_g/λ_s.

At this point a few words should perhaps be included regarding the basis on which errors are stated. In the present report, all uncertainties will be given as probable errors (P.E.), which means that there is a 50-50 chance that the true value lies within the stated limits. This was the criterion always used by BIRGE and employed by DUMOND and COHEN in their first two reviews. In their most recent work they use standard deviation (1.48 P.E.); this difference is primarily one of personal preference.

Probable error is rigorously defined only for statistical errors, e.g., one resulting from the use of a Geiger counter for a finite counting time. When systematic errors are important, as is usually the case, many workers prefer to give a « limit of error ». There are a few instances in which this term may be strictly applicable. For example, the width of a gap which is measured by means of very accurate feeler gauges is known to lie somewhere between two values; no further information is known on error distribution. However, in most cases of systematic error, there is a large subjective factor in the estimate of either P.E. or limit of error. There is ample evidence that the latter term as used in practice gives no ironclad guarantee that the true value must lie within the stated limits. Hence it seems quite as justifiable to use P.E. even in the case of systematic error. It may be defined as an estimate such that the experimenter feels it is equally probable that the actual systematic error is greater or is less than the P.E. (Theoretically a standard experimenter might be found by choosing one whose estimates on many experiments have proven high and low equally often.) The P.E. is frequently obtained from a stated limit of error by arbitrarily dividing by three. While this rule has not been followed blindly in the present report, it is approximated in many cases.

B) Experiments.

1. – Introduction.

A brief description will now be given of some of the various types of experiments used to determine the atomic constants. Only a few of these are sufficiently accurate to play an important part in fixing the precise numerical values of the constants today. However, the others are still of value in confirming the results of the more precise experiments or in pointing out possible sources of systematic error in them. The odds are about 20 to 1 that the result of an individual experiment should not differ from the true value by

more than three times its probable error. When such a disagreement exists and can not readily be explained, there is cause for concern, regardless of the actual magnitude of the probable error. Thus many older experiments are of more than historical interest. While the list given here is certainly not complete, it is believed to include the principal methods of determining the various constants over the past thirty years or longer.

For convenience in discussion, the experiments may be divided into three groups. The first consists of a number of experiments, usually simple in principle, which can be explained essentially in terms of classical theory. The second involves experiments which require some of the elementary ideas of quantum theory. The third class involves more complicated problems in quantum mechanics as well as the use of quantum electrodynamics.

As an aid to the reader who may wish to omit the earlier work, the experiments actually used in the present evaluation are starred (*). Most of these involve errors of the order of a few parts per million (ppm); the errors in the other experiments may be judged accordingly.

2. – Classical experiments.

2·1.* *Velocity of light.* – The velocity of light c is a most important physical quantity and has a proved a difficult one to evaluate properly. Excellent discussions of this topic include BIRGE's 1941 report [11] on the best values of the constants, a careful review by DORSEY [18] in 1944, and more recent survey articles by ESSEN [19] and MULLIGAN [20]. Various reviewers have determined what they considered the most probable values of c; the results are shown in Table I. It is clear that these values have fluctuated rather drastically, often by several probable errors.

TABLE I.

Reviewer	Date	Value (km/s)	Error (km/s)
BIRGE [8]	1929	299 796	4
BIRGE [11]	1941	776	4
DORSEY [18]	1944	773	10
VON FRIESEN [13]	1937	780	20
STILLE [14]	1947	778	20
DUMOND and COHEN [21]	1950	789.3	0.9
BEARDEN and WATTS [17]	1950	790.0	0.7
ESSEN [19]	1951	790	—
DUMOND and COHEN [21]	1952	792.9	0.6

The principal experimental values of the velocity of light are given in Table II.

TABLE II.

Experimenter	Date [a]	Value [b] (km/s)	Error [c] (km/s)	Method
ROSA and DORSEY [1]	1907	299 784	10	Ratio of units
MERCIER [2]	1923	782	30	Standing waves
MICHELSON [3]	1927	798	15	Rotating mirror
MICHELSON, PEASE and PEARSON [4] .	1935	774	4	Rotating mirror
MITTELSTAEDT [5] . .	1929	786	10	Kerr cell
HÜTTEL [6]	1940	771	10	Kerr cell
ANDERSON [7]	1937	771	10	Kerr cell
ANDERSON [8]	1941	776	6	Kerr cell
HOUSTOUN [9]	1950	775	9	Crystal grating
BERGSTRAND [10] . . .	1951 [d]	793.1	.2	Kerr cell
RANK, RUTH and VAN-DER SLUIS [11] . .	1952	776	15 [e]	Infra-red bands
RANK, SHEARER and WIGGINS [12] . . .	1954	789.8	3	Infra-red bands
PLYLER, BLAINE and CONNOR [13]. . . .	1955	792	6	Infra-red bands
ESSEN and GORDON-SMITH [14]	1948	792	3	MW cavity
ESSEN [15].	1950	792.5	1	MW variable cavity
HANSEN and BOL [16]	1952	789.5	.3	MW cavity
FROOME [17]	1952	792.6	.7	MW interferometer
FROOME [18]	1954	793.0	.3	MW interferometer
FLORMAN [19]	1955	795.1	3.1	RF interferometer
ASLAKSON [20]	1949	792.4	2.4	Shoran (radar)
ASLAKSON [21]	1951	794.2	1.4	Shoran (radar)

[a] Date of publication.
[b] Values in first group (8 experiments) are obtained from BIRGE [22]; in some cases corrections to original values have been made.
[c] Errors in first group are probable errors as given by BIRGE; those in second are those given by experimenters. (Probable errors unless otherwise stated in text).
[d] Mean value, reported by BERGSTRAND in 1951, of all his experiments to date.
[e] Original error revised by RANK in later paper [12].

[1] E. B. ROSA and N. E. DORSEY: *Bull. U. S. Bur. Stand.*, **3**, 433 (1907).
[2] J. MERCIER: *Ann. Phys. (Paris)*, **19**, 248 (1923); **20**, 5 (1923).
[3] A. A. MICHELSON: *Astrophys. Journ.*, **54**, 1 (1927).
[4] A. A. MICHELSON, F. G. PEASE and F. PEARSON: *Astrophys. Journ.*, **82**, 26 (1935).
[5] O. MITTELSTAEDT: *Ann. Phys.*, **2**, 285 (1929).
[6] A. HÜTTEL: *Ann. Phys.*, **37**, 365 (1940).
[7] W. C. ANDERSON: *Rev. Sci. Instr.*, **8**, 239 (1937).
[8] W. C. ANDERSON: *Journ. Opt. Soc. Amer.*, **31**, 187 (1941).
[9] R. A. HOUSTOUN: *Nature*, **164**, 1004 (1949); *Proc. Roy. Soc. Edin.*, A **63** (Pt. I), 95 (1950).
[10] L. E. BERGSTRAND: *Nature*, **165**, 405 (1950); *Ark. f. Fys.*, **2**, 119 (1950); **3**, 479 (1951).
[11] D. H. RANK, R. P. RUTH and K. L. VAN DER SLUIS: *Phys. Rev.*, **86**, 799 (1952); *Journ. Opt. Soc. Amer.*, **42**, 693 (1952).
[12] D. H. RANK, J. N. SHEARER and T. A. WIGGINS: *Phys. Rev.*, **94**, 575 (1954).
[13] E. K. PLYLER, L. R. BLAINE and W. S. CONNOR: *Journ. Opt. Soc. Am.*, **45**, 102 (1955).
[14] L. ESSEN and A. C. GORDON-SMITH: *Proc. Roy. Soc.*, A **194**, 348 (1948).
[15] L. ESSEN: *Proc. Roy. Soc.*, A **204**, 260 (1950).
[16] K. BOL: *Phys. Rev.*, **80**, 298 (1950); final corrected value of c was given in paper at High Frequency Measurements Conference, Washington, D.C., January 14, 1953.
[17] K. D. FROOME: *Proc. Roy. Soc.*, A **213**, 123 (1952).
[18] K. D. FROOME: *Proc. Roy. Soc.*, A **223**, 195 (1954).
[19] E. F. FLORMAN: *Journ. Research NBS*, **54**, 335 (1955).
[20] C. I. ASLAKSON: *Trasn. Amer. Geophys. Un.*, **30**, 475 (1949); *Nature*, **164**, 711 (1949).
[21] C. I. ASLAKSON: *Trans. Amer. Geophys. Un.*, **32**, 813 (1951); *Nature*, **168**, 505 (1951).
[22] R. T. BIRGE: *Reports on Progress in Physics*, **8** (The Phys. Soc., London, 1941), pp. 90-134.

The experiments at optical frequencies are all basically similar to Fizeau's toothed wheel experiment. (Brief descriptions are given by JENKINS and WHITE [22]). Basically this method employed a rapidly rotating toothed wheel which sends out pulses of light T seconds apart, each one containing many waves. The light covered a round trip over a known distance and was detected by the observer if it covered this path in some multiple of T and so passed through an opening in the wheel on its return. In later experiments the wheel was replaced by a many-sided rotating mirror or by a Kerr cell, which can be used as an electro-optical shutter at frequencies of the order of 10 mc. All of these experiments measure group velocity by determining the time to cover a given distance. ROSA and DORSEY determined c by measuring capacitance in electromagnetic units and calculating it in electrostatic units from geometrical dimensions, the ratio being c^2. MERCIER used a rf. oscillator with a measured frequency of the order of 100 mc and determined the wave length of these oscillations by measuring standing waves on wires. When this value was corrected to free space wave-length, it could be multiplied by the frequency to obtain c; this is thus a direct measurement of phase velocity.

The second group of experiments will now be considered in somewhat more detail:

a) HOUSTOUN performed an optical experiment using a piezo-electric crystal as a shutter; an rf field was applied which made it act as a diffraction grating during part of each cycle. The stated error of 9 km/s is purely statistical; no estimate of systematic errors is given. The method seems capable of considerable refinement.

b) BERGSTRAND's experiment employed the geodimeter, an instrument which he developed for measurement of length in surveying applications. It is based on a modulated Kerr cell; the photomultiplier tube used as detector was modulated by the same source (8.33 MHz). Elaborate precautions were used to eliminate or average out small errors, such as slight difference in transmission of various parts of the Kerr cell at a given instant. A major improvement lay in using a much longer base line (about 7 km) than in previous Kerr cell work; this greatly reduced the effect of any small uncorrected time lags in the cell and detector. BERGSTRAND gave .2 km/s as the standard deviation of the result. This appears to be stated less conservatively than some other (e.g., ESSEN's); but his result certainly seems to be by far the most accurate optical one.

c) The next series of experiments to be considered involves a combination of infra-red and microwave spectroscopy. For each vibrational state of a molecule, the rotational levels can be represented to high accuracy by

means of the rotational quantum number and two constants. If a large number of lines are measured for an infra-red vibration-rotation band (involving a transition between two vibrational level), these constants may be determined by a least squares adjustment; they are thus given in terms of wave numbers. These constants may also be found in frequency units by a microwave measurement of a transition between two rotational levels in the same vibrational state. Thus the same quantity is known in both frequency units and wave numbers; the ratio of these two values must be c.

RANK, RUTH and VANDER SLUIS carried out absorption measurement on an HCN band in the near infra-red (about .8 μm). Their error was originally given as 6 km/s; but in a subsequent paper [23] it is stated that the grating used may have introduced a systematic error of 14 km/s. In the RANK, SHEARER and WIGGINS experiment, involving an HCN band at about 1.6 μm, wave-lengths were measured with a Fabry-Perot interferometer; by small adjustments of air pressure in the interferometer it was possible to obtain an exact order of interference for the line to be measured. The error of 3 km/s appear to be the *sum* of four errors; if the probable error is calculated by the usual method, it will be less than 2 km/s. PLYLER, BLAINE and CONNOR measured a large number of lines in the CO band at 4.67 μm; they used both absorption and emission lines. The error given is standard deviation. The last two measurements both achieved higher accuracy than Rank's original experiment and both agree satisfactorily with other recent values of c. In all cases, the errors in microwave determinations of the band constants were much smaller than the spectroscopic errors.

d) Some of the most precise recent measurements have been carried out using evacuated resonant cavities with microwaves. In some respects, the resonant cavity may be thought of as the microwave analogue of the Fabry-Perot interferometer; a good general discussion of this type of experiment is given by MULLIGAN [20]. Briefly, a cylindrical metal cavity is employed; in order to obtain resonance the length must be some integral number of half wave-lengths. However, this wave-length is not the free-space wave-length although it has the same order of magnitude. It may be calculated in terms of free-space wave-length by solving Maxwell's equations; the relationship depends on which of many possible modes of oscillation is taking place. A small correction is applied for the finite Q of the cavity. Thus the free-space wave-length is found in terms of geometrical measurements, length and diameter; when the resonant frequency is determined, c may be computed. (If two resonant frequencies are measured for different modes, it is possible to eliminate one geometrical measurement, e.g., diameter.) This method essentially measures phase velocity; it eliminates the correction for index of refraction of air since the experiment is performed in vacuum.

ESSEN and GORDON-SMITH used a fixed cavity with the TM_{010} and TM_{011} modes of oscillation. A further refinement was introduced in the subsequent ESSEN experiment by having an adjustable piston at one end of the cylinder. The modes used were TE_{01p} and TE_{02p}, where p took various small integral values. In order to determine wave-length it was primarily important to know the difference in length between two resonant positions of the piston; the absolute length was not critical. This was an important feature since the results indicated that the electrical diameter might be about 2 μm greater than the geometrical value. ESSEN used two methods to correct for surface films and took the mean; there is a difference of about 1 km/s between these values. Values of c determined at three different frequencies checked to within .4 km/s. The probable error of 1 km/s appears to be conservative.

HANSEN and BOL performed an experiment similar to that of ESSEN and GORDON-SMITH. Despite the great care and ingenuity they used, there seem to be at least two possible sources of serious error. First the upper plate of the cavity had a mass of about 28 kg and produced considerable compression in the spacer rods as well as dents in the lower plate, which required important corrections. Secondly there may have been errors due to surface effects. To check this point, BOL repeated the experiment, taking special precautions to remove impurities, and found no appreciable change; this does not preclude a surface layer of silver of high resistivity, as found by ESSEN. ESSEN minimized this factor by using a variable piston and used a counterweight with the piston to avoid appreciable strain in his measuring gauge. Consequently there seems good reason to prefer ESSEN's result and to conclude that BOL's probable error should be raised considerably.

e) Several recent experiments are based on microwave interferometers. FROOME's first experiment used essentially a Michelson interferometer. The method is simple in principle and capable of high accuracy. However, it is complicated by diffraction effects, since the dimensions of the components are only a few wave-lengths. It is designed to employ spherical waves, but some corrections are necessary and the calculations are rather involved.

FROOME's second experiment, which employed a more symmetric arrangement of components, is shown in highly simplified form in Fig. 1. The carriage was set so as to obtain an interference minimum and then moved through about 81 wave lengths (about 1 m) and carefully set for a minimum. The distance was measured in terms of very accurately known length gauges, a micrometer being used for a small final adjustment. This was done for a series of ten different transmitter-receiver distances in order to obtain the diffraction correction. To further investigate diffraction effects, three series of measurements were made, one with convex plastic lenses in the horns, one with half lenses, and one without lens. Slightly different methods of making the dif-

fraction corrections were tried. Although these corrections amounted to as much as 100 km/s, the mean of different series taken with various lenses and various methods of diffraction correction checked within about 1 km/s. The final value given is based solely on the measurements using convex lenses. The stated error of .3 km/s is apparently based on standard deviations; this would imply a probable error of only .2 km/s.

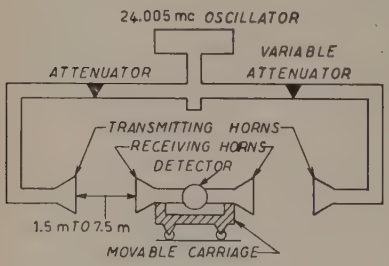


Fig. 1.

The FLORMAN experiment used the interferometer principle at a much lower frequency, 173 MHz. Since the wavelength is thus about 1.73 cm, it was decided to perform the experiment on a flat dry lake bed. Two receivers were placed 1.5 km apart, the distance being measured to about 1 ppm. A portable transmitter was then moved in a path encircling both and the maximum phase difference was noted. The 1.5 km distance was then divided by half of this difference (in seconds) to obtain the velocity of the waves. Corrections were made for ground effects and for index of refraction of air. The error was given as 3.1 km/s, including a systematic error of .7 km/s and a 95% confidence interval for the statistical measurements. This implies a probable error of about 1 km/s.

f) ASLAKSON has made several determinations of *c* by means of « Shoran » (radar) measurements of a number of base lines ranging up to 235 miles. This is apparently the only direct radio measurement of group velocity. The errors reported are statistical mean deviations. The principal error in the 1949 measurement was a « signal intensity correction », which was substantially eliminated in the 1951 work. The probable error of the second experiment appears to be about 2 km/s.

It is evident that all recent values lie in the vicinity of 299 793 km/s. The only glaring exception is the HANSEN and BOL result, which differs from this figure by about ten times its probable error. Reasons for this discrepancy have already been discussed and appear to provide a plausible explanation.

On the other hand, the older experiments, which are mostly optical ones, yielded Birge's average of 299 776 km/s. Among the optical experiments, only the Mittelstaedt and 1926 Michelson values may be considered in reasonable agreement with recent results.

Of course, the older experiments were much less accurate; for example, in the Michelson, Pease, and Pearson experiment, individual determinations were scattered over a range of 100 km/s. Systematic errors may have been considerably larger than estimated. BERGSTRAND [24] has recently studied the older optical work and reevaluated

the errors. For example, in the Michelson experiments he considers the variation in local atmosphere due to the expanding air blast from the turbine which drove the rotating mirror; an error of 8 km/s is ascribed to this in the evacuated pipe determination. However, it should be noted that Birge obtained an error of only 1.4 km/s by external consistency; this error is primarily determined by the agreement between different experiments. Even if all six older optical experiments are arbitrarily assigned equal weights, the resulting value of c is raised to only (299 779 $\pm$ 3) km/s, the error being determined by external consistency. Thus, while it is relatively easy to find additional possible sources of error in certain experiments, it is extremely difficult to explain why the statistical average was so far in error.

So far as is known to the writers, the only partial explanation put forward as to the direction of the errors in the older experiments was given by DAYHOFF [25]. He has pointed out that Anderson used the group index of refraction for 5 500 Å to correct results to vacuum although the photocell and light source employed probably had their maxima at a considerably lower wave-length. Correcting for this might increase the Anderson result in the order of 1-5 km/s. This point is well taken, but can at most account for a small part of the discrepancy.

Attempts to reconcile optical and microwave values of c thus depend chiefly on accepting Bergstrand's result and rejecting most other optical experiments. (There is some question as to whether the values obtained from infra-red bands should be classed as optical or microwave ones; they would appear to be essentially optical ones if the relation $E = h\nu$ can be regarded as certain). Hence there would seem some small room for doubt as to possible dispersion of light in vacuum.

Under the circumstances, it seems worthwhile to briefly mention some indirect evidence against such a variation. *a*) Measurements of velocity of γ-rays by LUCKEY and WEIL [26] and CLELAND and JASTRAM [27], with errors of the order of 1%, show no evidence of a difference in c at these extremely short wavelengths. *b*) Observations on eclipsing binary stars [28] fail to show any conclusive evidence of dispersion in the visible region. *c*) The Rydberg constant, which varies inversely as c, is used in both the optical and X-ray regions; this provides a rather sensitive test.

Thus, while the direct evidence for any variation in c seems inconclusive, the indirect evidence against it appears rather strong. The question then arises as to whether the older optical values should be considered at all. The only ones in this group which are comparable in accuracy with any recent results are the Michelson, Pease and Pearson and the Anderson 1941 values. In both cases the errors were revised by Birge; in fact, the MPP paper [see (4) in Table II] did not contain even an estimate of systematic error. Dorsey took a more pessimistic view than Birge in both cases; he estimated that the MPP systematic error might be as high as 10 km/s. In light of our present knowledge, it would seem that Dorsey's view is fully justified. Thus, in the present evaluation of c, it seems reasonable to include the infrared experiments (with errors of 3 and 4 km/s), but to reject all optical values except Bergstrand's.

If the experiments were weighted with the probable errors assigned by the experimenters, c would primarily be determined by the BERGSTRAND, HANSEN and BOL, and FROOME results. However, it seems preferable to adopt a system of somewhat arbitrary weights based on two factors: *a*) The stated probable errors with some modifications due to the reasons discussed above, particularly in the case of HANSEN and BOL, and *b*) the difference in methods used. It seems desirable to give comparable weight to several different methods (Kerr

cell, microwave cavity, microwave interferometer, radar, infra-red bands) even though not strictly justified on the basis of probable errors; this procedure gives some insurance against completely unsuspected systematic errors. The final evaluation is shown in Table III. In the case of RANK *et al.*, ESSEN, FROOME, and ASLAKSON, all but their *last* results are omitted and the entire weight given to the most recent values. Probable errors, computed from statements of the experimenters, are included only for comparative purposes.

TABLE III.

Experimenter	Value c_i (km/s)	P.E.	Weight w_i	Deviation d_i
BERGSTRAND	299 793.1	.14	5	+ .3
RANK, SHEARER and WIGGINS	789.8	3	1	— 3.0
PLYLER, BLAINE and CONNOR .	792	4	1	— .8
ESSEN	792.5	1	3	— .3
HANSEN and BOL	789.5	.3	1	— 3.3
FROOME	793.0	.2	5	+ .2
FLORMAN	795.1	1	2	+ 2.3
ASLAKSON	794.2	2	1	+ 1.4

$$\text{Mean} = \Sigma w_i c_i / \Sigma w_i = 299\,792.82 \text{ km/s}$$

$$(\text{P.E.})_{\text{ext}} = .6745 \sqrt{\Sigma w_i d_i^2 / (8-1) \Sigma w_i} = .34$$

If the HANSEN and BOL value is entirely omitted the result will be raised to 299 793.0 km/s. However, it will be retained in the present report and the result given as

$$c = (299\,792.8 \pm .4) \text{ km/s} \qquad (1 \text{ ppm}) .$$

If the above analysis is correct, c is probably the most accurately known of the principal atomic constants. It is therefore convenient to treat it as an auxiliary constant (i.e. consider it as exactly known); it is then assumed that experimental errors are uncorrelated through the use of c. In discussing the various experiments in the following sections, it will always be made clear how c is involved, if at all. However, the above numerical values of c will be used in stating the final results in cases where this will put the results more nearly in the form given by the experimenters.

It should be emphasized once more that the *direct* evidence against a variation of c between optical and microwave values rests primarily on BERGSTRAND's experiment. Since the microwave values are in such good agreement between themselves, further microwave work will probably not throw any additional light on this question. On the other hand, one more direct optical measurement confirming BERGSTRAND would do much to settle any lingering doubts.

2·2. *Electrical standards.* – The older studies of atomic constants usually included the conversion factors between international electrical units and the corresponding absolute quantities. On January 1, 1948 the old international system was abolished and all electrical measurements since then have been in terms of absolute units. At first glance it might seem that the experiments giving the old conversion ratios need no longer be considered in evaluating atomic constants. However, while the change has undoubtedly been a desirable step and reduced the multiplicity of electrical units, our knowledge of the constants still depends on the same experiments, regardless of this change in units. There are two reasons why they must be considered.

In the first place these results still contribute to the error in other experiments involving electrical measurements. The absolute electrical units are defined in terms of the mks mechanical units with the added provision that the permeability of free space is defined as $4\pi \cdot 10^{-7}$. Precise determination of absolute units in terms of these definitions is a very painstaking process and, in general, involves errors greater than those encountered in the intercomparison of electrical units. Thus the errors involved in precision electrical measurements hinge on the same experiments as before.

The second factor, which does not appear to have been considered seriously heretofore, is the possible correlation of various experiments through the common use of electrical standards. This would not occur with the present system *if* each experimenter made his own determination of absolute electrical units as needed. However, in practice, all workers in the United States depend on the Bureau of Standards for calibration of electrical standards. An error in these standards may thus be common to all such experiments (DuMond [29] has pointed out the dangers of such correlations in the case of λ_g/λ_s). With the precision now attainable in some experiments, the possible effect of this correlation should not be overlooked.

The various absolute measurements are summarized in reviews by Curtis [30] and Silsbee [31]. The determination of the ohm consists essentially of two steps. First a self-inductance or mutual inductance is very carefully constructed and its dimensions accurately measured. Since the permeability of free space is known by definition, the value of the inductance can be calculated from its geometry. Hence the reactance at any desired frequency may be computed. The second step consists in comparing this reactance with a standard resistance by means of a bridge or other suitable circuit; a number of different schemes have been used for this purpose. A recent measurement has been made by Thomas, Peterson, Cooter and Kotter [32] and was in good agreement with the previously accepted values. In his review Curtis quotes a weighted average error of 14 ppm for 8 experiments, which would imply an error of about 4 ppm in the mean value. This error appears to be a reasonable one.

The absolute determination of the ampere depends essentially on measuring the force between two conductors carrying the same current. The usual procedure has been to use three coaxial coils in series with the middle one movable and attached to the arm of a balance; frequently two such sets were employed, one at each end of the arm. A recent experiment by Driscoll [33] uses a Pellat balance, which uses a large stationary horizontal coil and a small movable vertical coil near its center; the movable coil is subjected to a torque rather than a force. The measured current is passed through a standard resistor and used to calibrate the standard cell. However, the determination of other currents in terms of these standards does not depend on the knowledge of the ohm in absolute units, but only requires that the standard resistor and cell do not drift with time. The three most accurate measurements quoted by Curtis in his review yield an error of the mean of only 2 ppm, but some of the values he rejected were off in the order of 100 ppm. It should be noted that there was a discrepancy of 3 ppm between this average and the conversion factor finally adopted in converting standards

to absolute units. The recent Driscoll determination differed from the accepted standards by 7 ppm with the experimental error estimated at 8 ppm. (The discrepancy quoted in the Driscoll abstract was 19 ppm, but this was revised to include a correction for current distribution in the smaller coil due to a change of resistance with mechanical stress). The probable error in the electrical measurements, including small drifts in the average voltage of the standard cells, would appear to be about 5 ppm. To this there must be added the error in the acceleration of gravity, since it is necessary to know g to measure force in terms of known masses. The comparison of the various determinations of g given by DRYDEN [34] would seem to indicate a probable error of about 3 ppm. The total error then becomes 6 ppm.

Thus the uncertainties in the various electrical units may be estimated as follows:

ohm	4 ppm
ampere	6 ppm
volt	7 ppm

The error in the volt is, of course, found by combining the errors of the first two measurements. These errors represent the highest accuracy obtainable in electrical measurements assuming perfect calibration of experimental measuring devices in terms of standards. In view of these errors, the correlation problem is not yet too serious a one, as will be evident from the following sections. However, it may soon be of greater importance and should be carefully kept in mind in future evaluations of the constants.

2·3.* *Electrochemical measurement of the faraday.* – The faraday may be determined by measuring the amount of a known electrolyte which is deposited when a measured quantity of electric charge has flowed through a coulometer (electrolytic cell). Early experimental work on silver and iodine was carried out by ROSA, BATES, and VINAL [35, 36]. At the time, the ampere was legally defined in terms of the electrolysis of silver, and there was strong emphasis on obtaining excellent reproducibility. This was indeed attained but there was a serious disagreement between the silver and iodine values of the faraday. There are at least four suspected sources of error: (1) the atomic weights used in the calculations may be incorrect, (2) the material deposited on the cathode may have inclusions of small pockets of liquid, (3) some of the material deposited on the cathode may redissolve in the solution, and (4) there may be partial isotopic separation.

The value of the faraday in the old international units depended only on the atomic weight of silver and the definition of the ampere. Hence in principle the experimental part consisted of calibrating standard cells in terms of an ideal silver coulometer and holding these standards constant through the years. Taking the atomic weight of silver [37] as 107.89 and using the conversion factor of .999835 abs. ampere/NBS int. ampere [38] then gives $F = 9651.3$ emu/eq. (The error in atomic weight may be of the order of .01% due to uncertainty as to the relative abundance of the two isotopes of silver.) Making similar corrections to the iodine values of the faraday [35]

using recent mass spectroscopic data for the atomic weight [39] yields $F = 9651.8$ emu/eq. Iodine has only one isotope and the error in its atomic weight appears negligible here. Also, in this experiment, a careful effort was made to eliminate errors of types (2) and (3) by checking the loss of iodine at the anode against the amount gained at the cathode. The limit of error for the chemical measurements appears to be about 50 ppm, which implies a probable error of roughly 20 ppm. When this is combined with uncertainties in electrical measurements, the resulting probable error should be in the order of 30 ppm.

CRAIG and HOFFMAN [40] have recently made a new determination of the faraday, using the electrolysis of sodium oxalate ($Na_2C_2O_4$). H_2 gas was given off at the cathode, there being no deposit in the usual sense. They weighed the total amount dissolved and determined by titration the amount remaining after a run. This procedure obviously eliminates errors of types (2) and (3); since titration depends on the number of moles but not the molecular weight, it also removes errors of type (4). It is, of course, necessary to know the exact purity of the compound dissolved. CRAIG and HOFFMAN used samples with purity certified as 99.96%. This involves an uncertainty of about 50 ppm. The impurities are analyzed and found to be inert in the reaction. At the time of the experiment there was a serious discrepancy between the chemical atomic weight of sodium and the mass spectroscopic value; this has now been removed by a revision of the chemical value [41]. Hence the Craig and Hoffman value becomes 9651.1 emu/eq. The present situation is summarized by them [42] as follows: (1) The purity of the sodium oxalate is thought to be slightly lower than the certified value. (2) There is some variation in F with current in the oxalate coulometer (due perhaps to a competing reaction) which suggests the need for extrapolation to infinite current. (3) These corrections are in opposite directions and it is impossible at the present time to estimate the correction of the combined effect.

From the above discussion, it seems evident that all three experiments are in reasonable agreement. The precise errors are difficult to estimate. If the three are averaged (giving half weight to the silver value because of the greater uncertainty in atomic weight), the resulting value is $(9651.42 \pm .15)$ emu/eq, where the error is computed by external consistency. Since the weighting is somewhat arbitrary and since all the experiments have some errors in common, for example the accuracy of electrical standards in absolute units, the error will be doubled and the result given as

$$\frac{Ne}{c} = (9651.4 \pm .3) \text{ emu/eq} \qquad (30 \text{ ppm}).$$

2·4. *Millikan oil drop.* – This well-known experiment consisted in measuring the charge on a single oil drop by means of the force exerted on it by an electrostatic field.

The rate of fall of the drop through a viscous fluid (air) was then given by Stokes' Law plus small experimentally determined corrections. The charge so determined was always approximately an integral multiple of an elementary charge, i.e., the charge of the electron. The experiment is described in many general physics texts, e.g., SEARS and ZEMANSKY [43]. For some time newer values derived from X-ray experiments of BEARDEN and others were in serious conflict with the oil drop results; the problem was apparently resolved by new determinations of the viscosity of air. The situation as of 1945 is well summarized by BIRGE [12]; he obtained $e = (4.8130 \pm .0075) \cdot 10^{-10}$ esu as an average of oil drop determinations by MILLIKAN [44], HOPPER and LABY [45], BÄCKLIN and FLEMBERG [46], and ISHIDA, FUKUSHIMA and SUETSUGU [47].

Subsequently, according to a footnote in a later paper by HOPPER [48], ISHIDA discovered an error of about 1% in voltage measurement. This would lower the Birge value to about $(4.804 \pm .008) \cdot 10^{-10}$ esu, in excellent agreement with other values of e. Unfortunately in this same report Hopper discusses a correction to Stokes' Law due to the proximity of the condenser plates and, using this correction in a new experiment, obtains $e = 4.8259 \cdot 10^{-10}$ esu (with the Birge figure for viscosity of air). While he claims greater internal consistency with this correction, it leaves the various experiments in serious disagreement. He believes the results may imply a lower value of the viscosity of air than now accepted. Another possible source of error pointed out by ISHIDA [49] lies in the facts that many drops are oblate spheroids rather than spheres.

If Hopper's corrections are accepted, the resulting mean appears to be close to 4.82 esu. On the basis of internal consistency as well as comparison with other methods of finding e, there seems to be reason to suspect some systematic error in his work and to reject his result. Since the oil drop method has comparatively low accuracy, it does not seem necessary in the present report to pursue the question further and attempt a more critical analysis of the conflicting data.

2·5. *e/mc by deflection methods.* – The so-called e/m experiments may be divided into three classes, as has been pointed out by DUMOND and COHEN [16]. One class gives a direct determination of e/mc (e/m in emu); the other two yield e/mc only with the use of the faraday. The measurement of the faraday is subject to numerous errors, as previously discussed; hence it can not be treated as an accurately known auxiliary constant. Thus it is important to separate these three categories. The deflection experiments now to be considered form part of the first class; the other data will be discussed in the proper section of Part B, **3**. The following data include corrections to absolute electrical units; most of the corrected figures are taken from DUMOND and COHEN [16].

Early measurements were carried out in the well-known work of Sir J. J. THOMSON [50]. The principle of his method is described in many texts, e.g., SEARS and ZEMANSKY [43]. It consists essentially in measuring the deflection of a beam of electrons in a known magnetic field and then finding the electrostatic field which will just cancel this deflection.

To secure greater accuracy the obvious modification in Thomson's method is to observe the deflection of electrons through a circle, or through many revolutions, rather than a small arc. This is facilitated by the well-known fact that an electron in a uniform magnetic field revolves in a circle with uniform angular velocity $\omega = He/mc$, independent of its velocity. (Since this is the principle of cyclotron operation, this expression is often referred to as the cyclotron frequency of the electron). DUNNINGTON [51] devised a very careful experiment in which an electron beam traveled through

a narrow circular ring of 340° in a uniform magnetic field. The electrons were accelerated by a high frequency voltage at the beginning of the trajectory and either accelerated or decelerated by the same voltage source at the end; this gave a resonance dip in the current when the time of flight was exactly one cycle. The field was adjusted for resonance and measured by means of the current in the solenoid used; ω was determined from the known frequency and angle; thus e/mc was calculated. The principal difficulty lay in the formation of surface charges and corresponding spurious potentials (sometimes 10 to 20 V) on the walls of the evacuated chamber. DUNNINGTON attempted to allow for this by extrapolating to infinite energy; this correction was of the order of 5 parts in 10^4. SHAW [52] has criticized this on the basis of his own work with surface charges and questioned the assumptions on which the extrapolation was based. Dunnington's result was $(1.7598 \pm .0004)\cdot 10^7$ emu/g; if Shaw's criticism is correct, the error should be increased to perhaps .0010.

SHAW [52] measured e/m in a rather complicated method employing a cylindrical condenser with a radial electrostatic field and an axial magnetic field. Under these conditions he showed that a beam of electrons would be focused by the combined fields if it traveled through a circular arc of about 127°. In general, electrons struck the collector for two different velocities or for none; however, with the proper combination of electric and magnetic fields, they struck the collector for a unique velocity. (The velocity of the electrons was varied by changing the accelerating voltage). Under these conditions it was possible to calculate e/mc from the measurements of the fields and the radius of the orbit. Shaw's value was $(1.7582 \pm .0013)\cdot 10^7$ emu/g.

PERRY and CHAFFEE [53] measured e/mc by a direct velocity determination. An electron beam was accelerated by a high voltage E, from which the energy of each electron could be calculated in terms of e. It was then passed between two pairs of electrodes a known distance apart, to which a radio frequency voltage was applied. Electrons came through to a fluorescent screen without deflection only if they covered this distance in exactly one cycle of the r.f. Since the frequency could be accurately measured, the electron velocity was thus obtained and e/mc computed from the relation $Ee/c = mv^2/2$ (with proper relativistic correction), where E is in statvolts. The result was $(1.7611 \pm .0010)\cdot 10^7$ emu/g, which seems rather high. There may have been some error due to an axial magnetic field needed to focus the beam and secure sufficient intensity; they describe this as an undesirable but necessary feature. KIRCHNER [54] performed a similar experiment with a resulting value of $(1.7590 \pm .0009)\cdot 10^7$ emu/g.

The Busch method makes use of the focusing property of a magnetic field parallel to the direction of a beam of electrons. The electrons are accelerated through a known voltage and then emerge through a small aperture in the anode as a slightly divergent beam. Assume that the velocity is principally directed along the z axis with small random components in the xy plane. If a magnetic field is applied along the z axis, the electrons will revolve in circular orbits in the xy plane with angular velocity $\omega = He/mc$. Since they all have nearly the same velocity v along the z axis, they will return to a focus on the axis after traveling a distance $l = 2\pi v/\omega$. v is found from the accelerating voltage (as in the previous experiment) and e/mc calculated. The method was first used by BUSCH [55]. More accurate determinations by WOLF [56] and GEODICKE [57] gave $(1.7590 \pm .0018)\cdot 10^7$ emu/g and $(1.7587 \pm .0008)\cdot 10^7$ emu/g respectively.

If Dunnington's error is increased as previously explained, all results except Wolf's have roughly the same error, viz., $.0010\cdot 10^7$. When all are weighted equally the resulting mean is $1.7593\cdot 10^7$. The error is about $.0004\cdot 10^7$ by internal consistency and slightly less by external consistency. Inclusion or omission of the Wolf result

makes no significant change. The result of all the deflection measurements may therefore be taken as

$$e/mc = (1.7593 \pm .0004)\cdot 10^7 \text{ emu/g} \qquad (230 \text{ ppm}) .$$

2·6.* *Avogadro's number* (*X-ray crystal density method*). – Avogadro's number N is defined as the number of molecules per mole (gram molecular weight). Thus, for a substance with molecular weight M, the mass of each molecule is M/N. If this substance has a perfect cubic crystal structure with unit cell of length d containing f atoms its density ϱ is fM/Nd^3. For a crystal such as calcite, where the unit cell is a rhombohedron, d^3 must be multiplied by φ, the volume of a rhombohedron with sides of unit length. (This can be calculated in terms of the dihedral angle α between two faces of the unit cell.) Hence N is given by

$$N = fM/\varrho d^3\varphi .$$

Experimentally the problem of using this relation to obtain N reduces to a measurement of d and φ (i.e. α) by means of X-rays and an accurate determination of density and molecular weight.

This work has been reviewed at some length by BEARDEN [58] and BIRGE [12]. Several different crystals have been employed. However, since the calcite determinations appear to be the best, only calcite will be used here. Accurate determinations have been made by BEARDEN [59] and BROGREN [60]. BEARDEN determined the density of calcite by weighing crystals in kerosene and using Archimedes' Principle; the same crystals were later checked by the Bureau of Standards. The mean of these measurements together with one by DEFOE and COMPTON gives the value $\varrho = 2.71029$ g/cm³, which should be accurate to within 10 ppm. α is determined by reflecting X-rays from two faces of the crystal and φ is then computed. BEARDEN found $\varphi = 1.09594 \pm .00001$ at 20 °C. BROGREN obtained a value 20 ppm higher. (He also calculated a value 40 ppm higher based on a mean of five different measurements, including his own; but this appears to have given equal weight to less accurate determinations.) In the present calculation φ will be raised 20 ppm to 1.09596 (a mean of the BEARDEN [59], BROGREN [60] and TU [61] values) and assigned an error of 15 ppm. The molecular weight of calcite, when computed directly on the physical scale from recent mass spectroscopic date (see BROGREN [60] for details), is 100.119; the error is about 20 ppm due chiefly to uncertainty in the abundance ratio of calcium isotopes. However, the effective molecular weight is slightly higher due to impurities. BIRGE calculated from BEARDEN's data that this correction should be 31 ppm. BROGREN used an average based on both BEARDEN and STRAUMANIS to obtain 50 ppm. In the present work a correction of 40 ppm will be made and assigned an error of 20 ppm. This gives $M_{\text{eff}} = 100.123 \pm .003$ (30 ppm).

The distance d is measured by observing X-ray diffraction from calcite, using the Bragg Law. This involves a rather complicated three-dimensional phenomenon and is well described by COMPTON and ALLISON [62]. Briefly the results show that whenever a diffraction maximum occurs, it may be considered as arising by direct reflection from parallel planes passed through the atom in some simple manner. These are the so-called Bragg planes; their intercept on each crystallographic axis is the reciprocal of some integer (usually small in practice) times the length of unit cell along that axis. Waves scattered from all atoms in such a plane are in phase since they are produced by direct reflection; for a maximum it is also necessary that waves from each of the parallel planes reinforce one another. Fig. 2 shows that the necessary condition for this is

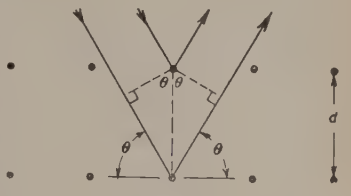


Fig. 2.

$$n\lambda = 2d \sin\theta ,$$

where n is an integer, d is the separation between planes, λ is the wave-length, and θ is the angle between the plane and the incident beam.

In early X-ray work it was soon apparent that the diffraction angle θ for X-ray wave-lengths could be measured much more precisely than the value of d was known. An arbitrary value for the grating space of calcite, d' (Siegbahn) $= 3029.51$ XU at 20 °C, has therefore been assumed for X-ray wave-length measurements and crystallographic work; the XU is approximately 10^{-11} cm. (This Siegbahn scale was originally based on rock salt with $d' = 2814.00$ XU at 18 °C, but it was soon found that calcite was a more suitable as a standard.) Since the value of d' is assumed, it has no probable error, except possibly 5 ppm due to temperature and index of refraction corrections and to variations between samples of calcite crystals. This grating constant d' may be regarded as the length of a cell containing one half of a calcite molecule (i.e. $f = \frac{1}{2}$). It must still be multiplied by a conversion factor λ_g/λ_s to convert it to absolute units. Since λ_g/λ_s is also needed in other X-ray experiments, its determination should be treated as a separate experiment to avoid correlation between the various data; this point has been emphasized by DUMOND and COHEN [29]. The conversion factor λ_g/λ_s will be treated in the next section. The equation for N may be rewritten as

$$N' = N(\lambda_g/\lambda_s)^3 = fM/\varrho d'^3\varphi ,$$

where d' is the grating space in terms of the Siegbahn scale; in other words, N' would be the value of N if 1 XU were exactly 10^{-11} cm. When the various

values given above are inserted, the result is

$$N' = (6.06145 \pm .00022) \cdot 10^{23} \text{ mole}^{-1} \qquad (38 \text{ ppm}) .$$

A rhombohedral crystal may also be referred to a hexagonal set of axes. The volume $d^3\varphi$ must then be replaced by $3a^2c\sqrt{3}/2$, where c is measured along the optic axis and a lies in a plane perpendicular to it. This makes it possible to compute N (or N') without measuring the angle α. BROGREN used a «unit cell» containing 18 molecules and found $a' = 4997.97$ XU and $c' = 17.02599$ XU (corrected to 20 °C), both having errors of 6 ppm. These results yield $N' = (6.06140 \pm .00021) \cdot 10^{23}$. VAN BERGEN [63] also measured grating constants in the hexagonal system. Using a «unit cell» of 36 molecules, he then obtained, at 20 °C, $a' = (9959.93 \pm .05)$ XU and $c' = (8513.06 \pm .06)$ XU. The corresponding value of N' is thus found to be $(6.06136 \pm .00021) \cdot 10^{23}$.

The agreement between results in the rhombohedral and hexagonal systems gives a good check on the various X-ray measurements involved. However, the major error, i.e., that of the molecular weight of calcite, is not eliminated. The mean value of N' will be taken as

$$N' = (6.0614 \pm .0002) \cdot 10^{23} \text{ mole}^{-1} \qquad (33 \text{ ppm}) ,$$

with the error substantially the same as for the individual values above.

This value may be compared with a value of $N' = (6.06178 \pm .00023) \cdot 10^{23}$ obtained by BIRGE [12], using data for five different crystal—calcite, diamond, NaCl, LiF, and KCl. Since the value given above for calcite differs from Birge's figure by almost twice his probable error, it may appear to be rather questionable to discard data for the other four crystals. However, a considerable part of the discrepancy is due to the rock-salt (NaCl) data, based on the work of TU [61]. The available data on NaCl is not in good agreement. An early measurement of Siegbahn gave a value of d 126 ppm higher than TU while STRAUMANIS obtained one 20 ppm lower. A more recent determination by VAN BERGEN [63] yielded a value 78 ppm higher with the error quoted as onlu 11 ppm. These wide variations may be due to a mosaic structure of NaCl as described by RENNINGER [64]. If VAN BERGEN's result were used instead of TU's, the N' obtained from NaCl would be the lowest of the five crystals instead of the highest and the Birge average would drop to 6.06150. On the other hand, if all NaCl data are omitted his average would be 6.06164. Thus the discrepancy is reduced to one probable error or less. When it is also recalled that the present analysis for calcite includes the BROGREN and VAN BERGEN work as well as recent mass spectroscopic data on atomic weights and abundances, none of which were available to BIRGE, it seems quite justifiable to adopt the present calcite value.

2·7.* *Ruled grating measurement of X-ray wave-lengths.* – The conversion factor λ_g/λ_s between XU and absolute units (milliangstroms) is found directly from measurement of X-ray wave-lengths by ruled gratings. At X-ray wave-lengths the index of refraction is less than unity and therefore total reflection occurs for X-rays incident on a grating from air or vacuum. (The simple theory must be slightly modified if absorption is appreciable.) It is only with total reflection that a grating is practical for use with X-rays; this means that the incident beam must strike the grating at a small glancing angle of the order of 1°, which corresponds to 89° angle of incidence in optical terminology. The wave-length is calculated from the usual optical formula $N\lambda = d \sin\theta$.

ECKART [65] has investigated the possibility of systematic errors (due, for example, to refraction, multiple scattering, and surface waves) when the above equation is used for an ideal grating at X-ray wave-lengths. He concluded that no appreciable error arises from these causes.

Precision grating measurements suitable for calculating λ_g/λ_s have been carried out by BEARDEN (5 results). BÄCKLIN, SODERMAN, and TYREN (4 results). Most of these experiments have been discussed by BIRGE [12] and in greater detail by BEARDEN [58]; however, BIRGE gives only one of TYREN's values, while BEARDEN's paper omits these entierly.

The various X-ray lines used in the above experiments were Cu-K_α, Cu-K_β, Cr-K_α, Cr-K_β, Si-K_α, Al-K_α, Mg-K_α, and Na-K_α, the wave-length region covering roughly 1 to 12 Å. BEARDEN and BÄCKLIN used plane gratings and determined absolute wave-length by directly measuring the grating space d. SODERMAN and TYREN, on the other hand, employed concave gratings and compared higher orders of X-ray spectra with first order spark spectra of various elements (e.g. the Lyman series of hydrogen-like ions, which could be calculated theoretically and required only a small experimental correction). The various results cover a spread of 130 ppm and show good agreement in view of the errors given, usually about 50 ppm.

Using his own data plus BÄCKLIN's and SODERMAN's, BEARDEN [58] obtained a mean of $\lambda_g/\lambda_s = 1.002\,03 \pm .000\,01$ (10 ppm), while BIRGE [12] later gave $1.002\,03 \pm .000\,02$ (20 ppm) with the inclusion of TYREN's Al-K_α measurement. It should be noted that the first four BEARDEN experiments have some systematic errors in common (estimated at 40 ppm) and are thus somewhat overweighted in the above averages since they are considered independent observations. In the conclusion of his paper, TYREN [66] recommended 1.002 01 as the best average of all experiments and SIEGBAHN [67] supported this view. After prolonged study the X-ray Analysis Group of the Institute of Physics adopted 1.002 02. In reporting this decision, BRAGG [3] states that the value is believed to be correct to within .003%; this is probably intended as a limit of error. In the present report, this last average will

be used with the probable error given by BIRGE, i.e.

$$\lambda_g/\lambda_s = 1.002\,02 \pm .000\,02 \qquad (20 \text{ ppm}) .$$

As BIRGE pointed out, the external consistency of the data suggests that this error is quite conservative; this remains true when the TYREN experiments are used.

2·8.* *Atomic mass of the proton and other atomic masses.* – The atomic mass of the proton enters into the calculation of atomic constants at several points. It has been determined by two principal methods. The first is by means of mass spectrometric measurements of « doublets », i.e. two ions which have almost the same e/M value. Thus the corresponding mass spectrographic lines will lie close together; in practice, this means that the small difference in mass can be measured to high accuracy. A commonly used set of three such doublets which yields the mass of the proton in terms of the standard ^{16}O is $(^1H)_2$—^2D, $(^2D)_3$—^{12}C, $^{12}C(^1H)_4$—^{16}O.

The second method forms an interesting contrast to the first; it makes use of energy differences determined from nuclear reactions to compute mass differences. While such measurements are not highly precise, they are only used to determine a small correction to the mass, i.e., the amount by which $^{16}O/M_H$ differs from the integral value 16. Thus, when a large number of such reactions furnishing various paths from ^1H to ^{16}O are used, a least squares solution can yield an accuracy comparable to that of mass spectroscopic determinations.

Recent data on the atomic mass of hydrogen have been summarized in a review by DUCKWORTH, HOGG, and PENNINGTON [39] and are shown in Table IV together with a new value computed by DRUMMOND [68].

TABLE IV.

Experimenter	Date	Method	$M_H \cdot 10^6$ (physical scale)
BAINBRIDGE	1947	Prewar mass spectroscopic data	1 008 128.3 ± 2.8
EWALD	1951	Mass spectrometer	41 ± 2
COLLINS, NIER and JOHNSON	1952	Mass spectrometer	46 ± 3
OGATA and MATSUDA . . .	1953	Mass spectrometer	45 ± 2
MATTAUCH and BIERI . . .	1954	Mass spectrometer	45.9 ± .5
LI *et al.*	1951	Nuclear reactions	42 ± 3
DRUMMOND	1955	Weighted average	44.0 ± .7

A good discussion of the work in mass spectroscopy and errors in the older measurements is found in the proceedings of the Symposium on Mass Spectroscopy [69] at the Bureau of Standards in 1951.

It is evident that the older data used by BAINBRIDGE probably contained serious systematic errors while the last six values concur reasonably well. The good agreement between the mass spectroscopic work and the nuclear data is very encouraging. The DRUMMOND average is obtained from a least squares evaluation of atomic masses, based on both nuclear and mass spectroscopic data, including all the above work except that of MATTAUCH and BIERI.

The present report is intended primarily as a study of atomic constants, rather than nuclear ones. Consequently the following scheme will be adopted without a more detailed study. The DRUMMOND value will be given a weight of three and the MATTAUCH and BIERI value a weight of unity. (This assigns a considerably higher weight to the DRUMMOND result than indicated by the relative errors, yet it appears justified on the ground that his study includes a considerable number of experiments employing two quite different principles.) The error will be conservatively set as .0000010, slightly higher than either the DRUMMOND or MATTAUCH and BIERI error. This accuracy of 1 ppm is still ample for the purpose at hand. Thus the result becomes

$$M_{\mathrm{H}} = (1.0081445 \pm 0000010)\ \text{amu (physical scale)} \qquad (1\ \text{ppm}).$$

The atomic mass of the proton is now readily found by subtracting the atomic mass of the electron, Nm. Since the latter is only a small correction, it need not be known to high accuracy. Thus the source of this datum is not critical and no appreciable error is introduced by it. The result is:

$$M_{\mathrm{p}} = (1.0075957 \pm .0000010)\ \text{amu (physical scale)} \qquad (1\ \text{ppm}).$$

Other atomic masses used (except silver) have been taken from or checked against the DUCKWORTH, HOGG, and PENNINGTON data. While several values are often given by the latter, the differences are generally not important in the present applications. One point should perhaps be mentioned in connection with the atomic mass of oxygen and the conversion factor r from chemical to physical state. The chemical scale is based on taking the atomic mass of oxygen as exactly 16, but does not specify its source. According to NIER [70] the chemical mass unit will have a mass of 1.0002783 amu. on the physical scale if atmospheric oxygen or oxygen from limestone is used as standard, but only about 1.000268 if the source is water or iron ore. Thus the conversion factor is no longer a matter of experiment, but rather of convention; according to WICHERS [71], it seems likely that $r = 1.000275$ will soon be adopted as a conventional value. This figure will be employed in the present report. The uncertainty in abundance of oxygen isotopes affects the CRAIG and HOFFMAN measurement of the faraday and crystal measurements of Avogadro's number, but is not critical in either case.

2·9.* *Ideal gas constant.* – While not directly needed in the evaluation of most of the atomic constants considered here, the ideal gas constant is needed in obtaining one important derived quantity, i.e., the Boltzmann constant. The value of pV for an ideal gas at 0 °C and zero pressure is given as (2271.16 ± .04) J/mole (chemical scale) by the Subcommittee on Fundamental Constants of the Committee on Physical Chemistry of the National Research Council [72], the error being the standard deviation. This is determined by precision measurements on almost ideal gases to determine the virial coefficients and permit extrapolating to zero pressure. Converting to the physical scale and changing to probable error gives

$$(pV)^{p=0}_{t=0\,^\circ\mathrm{C}} = (2271.78 \pm .03)\cdot 10^7 \text{ erg/mole} .$$

The absolute temperature at 0 °C is now known by definition. The Tenth General Conference on Weights and Measures [73] adopted a proposal originated by KELVIN in 1854 and renewed by GIAQUE in 1949 to define the absolute temperature scale by a single fixed point. This was taken as the triple point of water and defined as 273.16 °K. The zero of the Centigrade scale had previously been defined as .01 °C below the triple point [74]; hence 0 °C is now exactly 273.15 °K. Thus the gas constant $R = pV/T$ becomes

$$R = (8.3170 \pm .0001)\cdot 10^7 \text{ erg/deg mole} \quad (12 \text{ ppm}) .$$

It should be noted that neither RT nor kT is really known any more accurately at 0 °C as a result of the new definition of the temperature scale. Under the old system the product RT at 0 °C was known far more accurately than either R or T. Since in practice correlation coefficients are not usually employed in calculating error, the error in RT at or near 0 °C appeared to be far greater than it actually was. With the new definition a good estimate of the error can be obtained without resort to correlation coefficients.

3. – Quantum experiments.

3·1. *Photoelectric effect.* – The first precision experiment to give h or h/e made use of the photoelectric phenomenon. The theory of this effect was first given by EINSTEIN. (See, for example, SEARS and ZEMANSKY [43] or MILLIKAN [44]). It is summarized by the equation

$$h\nu - \varphi = \frac{mv^2_{\max}}{2} = 10^8 V \left(\frac{e}{c}\right) ,$$

in which ν is the frequency of the incident light, φ is the work function of the material, and $mv^2_{\max}/2$ represents the maximum kinetic energy of an emitted electron. This energy

is in turn equal to $10^8 Ve/c$, where V is the minimum retarding potential necessary to stop the photoelectric current. Since $\nu = c/\lambda$ it is only necessary to plot V as a function of $1/\lambda$; the slope of the resulting straight line is hc^2/e. In practice, the situation is complicated by varying amounts of impurities on the photo-sensitive surface and by photoelectric emission from other surfaces due to scattered light.

MILLIKAN [75] performed a very careful experiment designed to eliminate these difficulties. He constructed an ingenious experimental setup in which a new surface could be machined on the photo-sensitive material while it remained in a vacuum tube. The materials used were sodium and lithium, which are sensitive in the visible region, while the anode was copper, which has a photoelectric threshold well in the ultra-violet; thus over a large range of frequencies scattered light had little effect. MILLIKAN obtained $6.57 \cdot 10^{-27}$ as the value of h, using $e = 4.774 \cdot 10^{-10}$ and 300 as the conversion factor between statvolt and volt. The value of c used in calculating frequencies is not given; it may perhaps be assumed that it was taken as $3 \cdot 10^{10}$ cm/s as in the voltage conversion. If the results are then corrected to absolute electrical units and the present value of c inserted, Millikan's work gives

$$h/e = (1.379 \pm .007) \cdot 10^{-17} \text{ erg s/esu.}$$

More recently LUKIRSKY and PRILEZEAV [76] performed an experiment with photoelectrons from Zn, Al, and Ni; they found $6.543 \cdot 10^{-27}$ erg s as the value of h with an error of .1% to .2%. The « reverse current » due to emission from the anode was not eliminated, as in Millikan's work, but experimental corrections were carefully made. Another photoelectric measurement was made by OLPIN [77]; he used sodium surface sensitized by a mixture of sulfur vapor and air, which was sensitive throughout the entire visible spectrum. His published value [78] of h was $6.541 \cdot 10^{-27}$ « correct to at least three significant figures ». However, a similar run with pure sodium gave $6.6 \cdot 10^{-27}$; while this is admittedly less accurate due to smaller frequency range, it is not clear why it was neglected entirely.

Since neither OLPIN nor LUKIRSKY and PRILEZEAV give the values of e and c which they assumed, it is impossible to determine precisely their experimental values of h/e. In any event their results are roughly .4% lower than Millikan's. While both results are given with lower errors than Millikan's, it is not evident that there is any essential improvement to justify the higher weight. In fact, with the corrections required in the LUKIRSKY and PRILEZEAV work, the contrary might be expected. It should also be noted that both MILLIKAN and OLPIN obtained higher values of h with sodium, which they rejected. DUBRIDGE [79] and ROEHR [80] have discussed the effect of thermal energies on the results. They point out that Einstein's equation, holds strictly only at absolute zero and can be in error by several hundredths of a volt at room temperature; however, the error in the slope $dV/d\nu$ may be considerably less. In light of all these considerations Millikan's value will be lowered by .2% and his error retained. Hence the result of the photoelectric measurements is

$$h/e = (1.376 \pm .007) \cdot 10^{-17} \text{ erg s/esu} \qquad (510 \text{ ppm}).$$

3·2. *X-Ray photoelectric effect.* — Photoelectric experiments may also be carried out with X-rays. In this case the electrons are ejected from the lower energy levels of the atom rather than the conduction band; consequently the equivalent « work function » is much greater. The energies of the emitted electrons are high enough so that they may be conveniently measured by the radius of curvature r in a uniform magnetic field. The velocity is then given by Hre/mc (neglecting a small relativistic correction which is required); the corresponding energy is then $(Hre)^2/2mc^2$. The in-

cident frequency ν is given by $(c/\lambda')(\lambda_s/\lambda_g)$ and the « work function » is approximately $(hc/\lambda_q')(\lambda_s/\lambda_g)$, where λ_q is the absorption edge for the ejection of electrons from the particular level involved and the primes denote measurement on the Siegbahn scale. The resulting equation is

$$\frac{e^2}{mh}(\lambda_g/\lambda_s) = \frac{2c^3}{(Hr)^2}\left(\frac{1}{\lambda'} - \frac{1}{\lambda_q'}\right),$$

λ_q' may be determined from measurements on the absorption edge as done by KRETSCHMAR [81] or eliminated by taking measurements at two values of λ' as done by ROBINSON [82]. These experiments are discussed at greater length by DUNNINGTON [15], who concludes that the latter method is more accurate. Robinson's results, when corrected for the present value of e, yield

$$\frac{e^2}{mh}(\lambda_g/\lambda_s) = (3.828 \pm .002)\cdot 10^{34}\ (\text{esu})^2/\text{g erg s} \qquad (520\ \text{ppm})\,.$$

ROBINSON did not give an error for the final average, but quoted .075% as a limit of error in an earlier report. It seems safe to reduce this at least to .05% as given above; this is still about five times the statistical error of the result.

3·3. *Ionization and excitation potentials.* – The so-called h/e measurements by means of measurements of ionization or excitation potentials are quite similar in principle to the photoelectric determinations. The energy necessary to ionize an atom or to excite a given level is determined in terms of wave-length λ by spectroscopy measurements; this same energy is then measured by determining the voltage V necessary to accelerate an electron so that it will just ionize or excite the atom in question. It follows that $hc/\lambda = 10^8 Ve/c$ or $h/e = 10^8 V\lambda/c^2$. The measurement of ionization potentials has been carried out by LAWRENCE [83] on Hg, and by VAN ATTA [84] and WHIDDINGTON and WOODROOFE [85] on He, Ne and A. DUNNINGTON [15] has analyzed this data and obtained an average h/e of $(1.3743 \pm .0035)\cdot 10^{-17}$ erg s/esu (the value of c assumed is somewhat different from the present best value; but this is unimportant in view of the error).

A much more accurate measurement, involving the excitation potential of He, has been carried out by DUNNINGTON, HEMENWAY, and ROUGH [86]. The appratus was quite similar to that used by DUNNINGTON [87] in his e/mc experiment and is shown schematically in Fig. 3. A magnetic field was applied perpendicular to the paper and was adjusted so that electrons emerging from the electron gun had the proper radius of curvature to just pass through the first slit system. A small amount of He was introduced in the gap between the slit systems. When the voltage between them was approximately zero (actually a small voltage V_0 was necessary to correct for contact emf and similar effects), electrons which did not collide with the atoms passed through the second system and reached the collector; thus a current maximum was obtained for V_0. When the voltage was raised by the amount of the excitation potential to a new value V, a second maximum occurred since electrons which lost enough energy

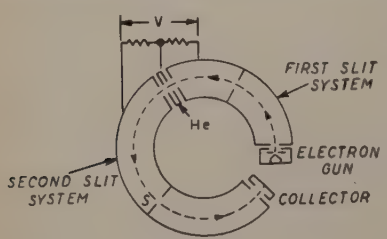


Fig. 3.

to excite one He atom by collision regained an equal amount in the gap and passed through the second slit system. The excitation potential measured was between the $1s^2\ {}^1S_0$ (ground state) and the $2p^1\ {}^1P_1$ levels. Dunnington's results gave

$$h/e = (1.379\,0 \pm .000\,2)\cdot 10^{-17} \text{ erg s/esu}\,.$$

The error given is principally a statistical *standard deviation*, but also includes an allowance for systematic errors in the electrical measurements.

Additional sources of error should perhaps be considered. Dunnington has noted three possible sources of error in voltage measurements: contact potential, space charge, and surface charge. Since only the difference between V_0 and V_1 is required, he eliminated any effect of contact potential as well as any surface or space charge phenomena which were independent of voltage. However, there is reason to think that the last two effects may have been voltage dependent. At voltage V_0, most of the electrons reached the collector; the few which had one or more collisions were stopped at slit S. At voltage V_1, those which had only one collision got through; all of the others were stopped by S. It seems quite plausible that this difference may have had some effect on space and surface charges in the second slit system. Of course, this effect may have been at least partially corrected for by an extrapolation to zero beam current which Dunnington made.

Dunnington also investigated other possible sources of systematic error. The apparatus was plated with gold at frequent intervals to reduce surface charge; he found some evidence of a change of about 140 ppm in the excitation potential during the average time delay between plating and taking a run; however, the error in this correction was such that he did not feel justified in including it. On the other hand, there was a small, but statistically significant, variation of ther esult with V_0; DUNNINGTON made a correction of .000 2 V to extrapolate from $V_0 = .004\,7$ V to $V_0 = 0$. Since there is no good explanation of this variation or even for the average value of V_0, it does not seem obvious that one obtains the true result by correcting to $V_0 = 0$ as determined by the potentiometer. A change of .01 V in the value of V_0 used would change the answer by 20 ppm. In the light of all these considerations it seems safer to make at least a small allowance for additional systematic errors and treat the uncertainty given by DUNNINGTON as a probable error rather than standard deviation. Thus his result is

$$h/e = (1.379\,0 \pm .000\,2)\cdot 10^{-17} \text{ erg s/esu} \quad (145 \text{ ppm})\,.$$

3·4. *Excitation potentials for discrete X-ray lines.* – A modified form of the method described in the last section can be used with X-ray spectra. When a metallic target is bombarded by high velocity electrons both a continuous and a discrete X-ray spectrum are observed. The latter is, of course, characteristic of the atoms of the target. The so-called K lines are produced when one of the two electrons in the innermost level is removed and another electron falls into its place with the emission of a photon. Clearly it is impossible to excite this radiation unless the bombarding electron has at least enough energy to raise a K electron to the lowest unoccupied level of the target. This energy is equal to $10^8 Ve/c$, where V is the minimum target voltage necessary to excite K lines.

The wave-length corresponding to this voltage may be determined from X-ray absorption measurements. When the frequency ν is raised to a value such that an X-ray photon can eject a K electron to the lowest unoccupied level, a sudden rise in the absorption coefficient of the material is noted; this « absorption edge » represents the desired wave-length. (Since neither this absorption edge nor the excitation voltage

is defined with perfect sharpness there is some uncertainty in deciding exactly what points on the two curves correspond to each other). The photon energy is then hc/λ; by equating this to the corresponding electron energy it follows that

$$(h/e)(\lambda_s/\lambda_g) = 10^8\lambda' V/c^2 ,$$

where λ' denotes wave-length on the Siegbahn scale.

Some preliminary results by this method were briefly reported by BEARDEN and SCHWARZ [88]. It is interesting to note that these results, which they then felt were less reliable than their measurements of the continuous X-ray spectrum, now appear to be their best value obtained at the time.

More recently NILSSON [89] completed an extended series of measurements of K excitation voltages for Fe, Co, Ni, and Cu. The absorption data needed was taken from BEEMAN and FRIEDMAN [90]. NILSSON gives a limit of error of about 450 ppm. The systematic errors in voltage measurement are combined as the square root of the squares, giving 230 ppm; other errors are added arithmetically to this. It seems safe to halve the voltage uncertainty in computing a probable error. Among the other errors, that in c^2 may be considered negligible while that in (λ_g/λ_s) does not appear in the present statement of the result. The uncertainty in locating corresponding points on excitation and absorption curves is given as 50 ppm; this estimate should probably be retained without change in the absence of a good theoretical explanation of the shape of the curves. When all remaining errors are combined by taking the square root of the sum of the squares, the probable error is about 138 ppm. The original data, as given by NILSSON in Table XXIII, has been recalculated with the present value of c; the result may be stated as

$$(h/e)(\lambda_s/\lambda_g) = (1.3766 \pm .0002)\cdot 10^{-17} \text{ erg s/esu} \quad (145 \text{ ppm}) ,$$

where the probable error can be considered rather conservative.

3·5. *High-frequency limit of continuous X-ray spectrum.* – The X-ray « h/e experiments » are essentially the inverse of the photoelectric determinations. A beam of electrons is accelerated by a known voltage and allowed to strike a metal target (the anode), where X-rays are produced. The maximum energy (i.e., the highest frequency) X-ray photon will be emitted when all of the energy of an electron is converted to radiation in a single collision. Thus is λ' is the wave-length of the high frequency limit on the Siegbahn scale, the resulting equation is

$$(h/e)(\lambda_s/\lambda_g) = 10^8\lambda' V/c^2$$

the same expression as was given in the previous section.

The most common procedure consists in setting an X-ray monochrometer for a given wave-length and observing the intensity as the voltage is varied about a small range near cut-off frequency; the resulting curve is called an isochromat.

Fig. 4 shows a typical isochromat for tungsten. The intensity is usually measured by a Geiger counter and must be corrected for the background count. The experimental curve does not, of course, show a perfectly sharp cut-off, but approaches the axis assymptotically. The usual way of locating the high frequency limit has been to take the point where the second derivative of isochromat is a maximum; this method was first proposed by DuMond and Bollman [91]. There is some experimental error involved, which depends on the number of counts for each point on the curve, as well as a possible theoretical error which will be discussed later.

Fig. 4.

Other possible sources of error are impurity films on the target, thermal emfs, ripple voltage, thermal velocities of electrons, and cathode work function. It has been shown by DuMond and Bollman [91] that an energy equal to the work function is supplied to each electron from the filament power supply; the work function voltage must therefore be added to the plate voltage. The correction is known quite accurately for tungsten, but varies in a rather unpredictable manner for an oxide cathode. Most of the errors just mentioned involve constant voltages and can be reduced by going to a high voltage.

The first precision experiment of this type was that of Duane, Palmer and Yeh [92]. However, the principal weight must now be given to three recent determinations (the figures quoted are the values of $10^8\lambda' V$ in cm emu):

a) In 1950 Bearden and Schwarz [93] obtained 12370.76 $\pm$ .50 as a mean of 9 determinations with Cu, Ni, Mo, Ta, Au, and W targets. (In computing the above error, the uncertainty in the work function has been lowered to 30 ppm.) Most of the work was done with an indirectly heated oxide cathode at 8 to 10 kV, although one run was taken with a tungsten filament and two at about 20 kV. A double crystal spectrometer was used.

b) In 1951 Bearden, Johnson, and Watts [94] performed a rather similar experiment with one major improvement; they used a tungsten filament which was heated during alternate half cycles of the 60 cycle supply and employed a « gating circuit » to record counts only during the half cycles when the filament power was off. Thus they obtained essentially a unipotential cathode with an accurately known work function. The target was also tungsten and runs were taken at 6 and 10 kV with wave-length as the variable. A third result was obtained by considering the difference in the high frequency limit for these two voltages. The mean of their values was 12371.09 $\pm$ .50. (The published result includes the Bearden and Schwarz value in the average

as stated in Fig. 3 of the BJW paper. This seems to have caused some confusion. DuMond and Cohen [1] used this final average and then introduced the B and S value as a separate item, thus effectively including the latter twice in their average.)

c) In 1953 DuMond, Felt and Harris [95] determined the high frequency limit at 24.5 kV for a tungsten target, by means of a curved crystal spectrometer. A tungsten filament was used with the same « gating circuit » arrangement employed by Bearden, Johnson and Watts. The result was 12370.02 $\pm$ .42.

If these three determinations are given equal weight, the mean value is (12370.63 $\pm$ .28) cm emu. As will be shown later in this report, this average is significantly lower than that implied by other experimental data. The discrepancy is also clearly shown in the DuMond and Cohen [1] evaluation of atomic constants though they do not consider the evidence strong enough to reject these X-ray experiments.

There are at least two causes which may account for this disagreement. The first is the thermal energies of the electrons; the average value is 2 kT and the most probable value is kT (see, for example, Millman and Seeley [96]). It can be shown that the correction should lie somewhere between these limits. For the oxide cathode used by Bearden and Schwarz kT should be of the order of .1 eV while for the tungsten filament used in the other experiments it is about .2 eV. In any case it will tend to raise the experimental value.

A more important correction may perhaps be required due to the method of determining the high frequency limit by the maximum second derivative [97]. In introducing this method, DuMond and Bollman [91] assumed that the ideal isochromat consists of a series of straight lines and intersects the axis with a finite slope, as shown by the solid line in Fig. 5.

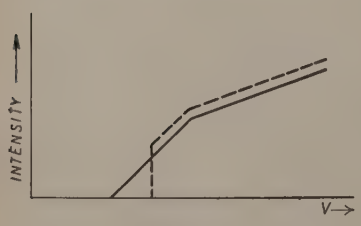


Fig. 5.

However, they also pointed out that, if a discontinuity exists at the high frequency limit, as shown by the dotted line, then the correct value is obtained by taking the maximum first derivative. They actually employed both methods and found a difference of about two volts; the observed isochromat could be reconstructed almost equally well on either hypothesis. For their final average a mean of the two values was used. While the difference between the two methods was not too important at the time, it becomes more critical with the accurate data now available. However, the second derivative method seems to have been accepted without much question in all recent work.

The assumption that the ideal isochromat consists of a series of straight lines with small discontinuities in the slope (the « knees » referred to by DuMond and Bollman [91]) is clearly no longer tenable. The recent work on tungsten by Bearden and Schwarz [93] and Bearden, Johnson, and Watts [94] shows, at 3 to 4 V above what is taken as the cut-off voltage, a peak followed by a distinct minimum; this was first noted by Ohlin [98]. Nijboer [99] has suggested there may be a range of forbidden energies between the Fermi levels of the target and that the intensity of an ideal thin-target isochromat may be zero in this region, as shown in Fig. 6. DuMond [100] also considered the problem and reached substantially the same conclusions. Thus the changes in slope near the cut-off voltage may well be of major importance.

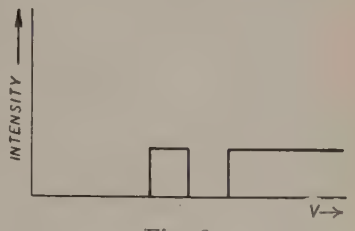


Fig. 6.

The original DuMond and Bollman theory postulated that the ideal thin-target isochromat had a discontinuity at the cut-off voltage and was constant for higher values, as shown in Fig. 7(*a*); they cited Sommerfeld's [101] work as theoretical justification. The thick-target curve was then considered as formed by the superposition of many thin-target ones with the electrons losing some energy in each layer. The resultant curve was a straight line intersecting the axis, which is indicated in Fig. 7(*b*). This analysis, as well as the later treatment by DuMond [100], assumed that the electrons lose energy continuously and that the energy loss at a given depth is the same for each electron.

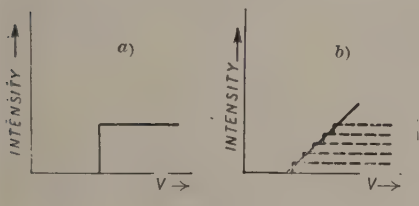


Fig. 7.

However, there is considerable evidence that energy losses occur largely in discrete steps of the order of 10 eV. Furthermore, even at depths where the average loss is much larger than this, there appear to be an appreciable number of electrons which have not undergone any measurable loss in energy. (See, for example, the work of Rudberg [102], Ruthemann [103], Lang [104], and Marton and Leder [105]). If these statements are correct, then a discontinuity should be expected at the cut-off voltage even for a thick target; the magnitude of this discontinuity is difficult to fix. Gerthsen and Albert [106] have developed a theory from a simple model with discrete energy losses and obtained an isochromat with a series of sharp steps. However, their work gave no explanation of the peaks and valleys which are observed and are qualitatively explained by Nijboer's model.

To form some estimate of how much the experimental results may be misinterpreted, a simplified example will now be analyzed. Assume that for any constant voltage V, with corresponding cut-off frequency $\nu_0 = 10^8 eV/ch$, the characteristic curve of intensity vs. frequency is

$$I(\nu, \nu_0) = \begin{cases} B + C(\nu_0 - \nu), & \nu \leqslant \nu_0, \\ 0. & \nu > \nu_0. \end{cases}$$

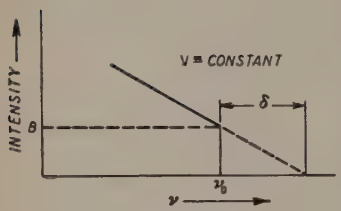


Fig. 8.

This is indicated in Fig. 8; the intercept of the projection of the characteristic is given by $\delta = \nu - \nu_0 = B/C$. B and C are considered constant over a small range of V. Assume further that the ideal isochromat is blurred only by the limited resolving power of the spectrometer and that this can be represented by the Gaussian function

$$f(\nu_s, \nu) = A \exp\left[-\left(\frac{\nu - \nu_s}{\sigma}\right)^2\right],$$

where ν_s is the frequency setting of the spectrometer. The observed intensity for given values of V (i.e., ν_0) and ν_s is now found by integrating $f(\nu_s, \nu) I(\nu, \nu_0)$ between the limits of 0 and ν_0; there is, of course, no radiation above ν_0. The resulting function $F(\nu_s, \nu_0)$ is thus

$$F(\nu_s, \nu_0) = \int_0^{\nu_0} A \exp\left[-\left(\frac{\nu - \nu_s}{\sigma}\right)^2\right] [B + C(\nu_0 - \nu)]\, d\nu.$$

The equation for an isochromat is obtained by holding ν_s constant and varying ν_0.

The maximum of the second derivative of the isochromat is found by differentiating $F(\nu_s, \nu_0)$ three times with respect to ν_0 (which is directly proportional to V) and setting the third derivative equal to zero. The result is

$$\frac{\partial F}{\partial \nu_0} = A \left\{ B \exp\left[-\left(\frac{\nu_0 - \nu_s}{\sigma}\right)^2\right] + \int_0^{\nu_0} C \exp\left[-\left(\frac{\nu - \nu_s}{\sigma}\right)^2\right] d\nu \right\},$$

$$\frac{\partial^2 F}{\partial \nu_0^2} = A \left[\frac{-2(\nu_0 - \nu_s)B}{\sigma^2} + C\right] \exp\left[-\left(\frac{\nu_0 - \nu_s}{\sigma}\right)^2\right],$$

$$\frac{\partial^3 F}{\partial \nu_0^3} = A \left[-\frac{2B}{\sigma^2} + \frac{4(\nu_0 - \nu_s)^2}{\sigma^4} B - \frac{2(\nu_0 - \nu_s)C}{\sigma^2}\right] \exp\left[-\left(\frac{\nu_0 - \nu_s}{\sigma}\right)^2\right].$$

The third derivative will vanish when

$$B\left(\frac{\nu_0 - \nu_s}{\sigma}\right)^2 - \left(\frac{\nu_0 - \nu_s}{\sigma}\right)\left(\frac{\sigma C}{2}\right) - \frac{B}{2} = 0.$$

If $B = 0$, it follows that $\nu_0 - \nu_s = 0$ and the maximum of the second derivative gives the true cut-off frequency. On the other hand, if $C = 0$, the above equation gives $\nu_0 - \nu_s = \pm \sigma/\sqrt{2}$; the negative root corresponds to the maximum of the second derivative. The first or second of the above cases will be approximated if σ is very large or very small respectively compared with the quantity δ in Fig. 8. In general, the desired root is

$$\frac{\nu_0 - \nu_s}{\sigma} = \frac{1}{2}\left\{\frac{\sigma C}{2B} - \left[\left(\frac{\sigma C}{2B}\right)^2 + 2\right]^{\frac{1}{2}}\right\}.$$

From this equation it follows that, for positive C

$$-\frac{1}{\sqrt{2}} \leqslant \frac{\nu_0 - \nu_s}{\sigma} \leqslant 0\,.$$

Thus, under the conditions assumed, the second derivative criterion can misinterpret the cut-off frequency by as much as $\sigma/\sqrt{2}$. It may easily be shown that the half width w of the Gaussian curve of the spectrometer is approximately $.83\sigma$; hence, roughly speaking, the second derivative method may misinterpret the result by w. Since $\nu_0 \leqslant \nu_s$, it follows that the voltage obtained by the second derivative method (i.e., that corresponding to ν_0) will be less than or equal to the true voltage for the setting ν_s. Therefore, if any error exists in this method, the calculated value of h/e will be lower than the true value.

Since precise structure of the ideal isochromat is not known, it seems unsafe to assume either that such a correction should be applied or that it should not: but it appears probable that the true value lies somewhere in this range. Thus it seems reasonable to apply a correction of $2kT + (hw/2)$ and increase the error appropriately. The details of these corrections are shown in Table V; the resulting unweighted mean of the three experiments is 12371.7. It will be noted that the BEARDEN, JOHNSON, and WATTS results are much more consistent after corrections.

It is not obvious what error should be assigned to the result. The correction factor is different for each experiment. On the other hand, the errors are not completely independent, since all involve the structure of the ideal isochromat (in most cases for a tungsten target). The correction to the DUMOND result is 139 ppm; the correction to BEARDEN and SCHWARZ and BEARDEN JOHNSON, and WATTS average 46 ppm and 59 ppm respectively. The average correction for the three experiments is thus 81 ppm; it seems reasonable to assign a probable error of 60 ppm due to the corrections. Combining this with the probable error of the mean due to other causes (23 ppm) gives a total error of 64 ppm. When the result stated in the preceding paragraph is divided by c^2, the final value now becomes

$$(h/e)(\lambda_s/\lambda_g) = (1.37653 \pm .00009)\cdot 10^{-17} \text{ erg s/esu} \qquad (65 \text{ ppm})\,.$$

If the first derivative criterion is applied, the change in the experimental values is in general considerably greater. In most cases the shift is too large to be plausible since the observed intensity should be essentially zero when the wave-length setting of the spectrometer is below cut-off by several half-widths. The shape of the curves near the maximum of the first derivative is probably influenced by the same mechanism producing the peaks and valleys. It seems unlikely that the present curves can be interpreted with high accuracy until a better theory is found to explain the form of the isochromats.

TABLE V. – *Corrected values of « h/e experiments ».*

Experiment	Voltage (kV)	Runs	kT (eV)	w (eV)	$2kT + hw/2$	Correction (ppm)	$(hc^2/e)(\lambda_s/\lambda_g)$ (cm emu) Original	Corrected
BEARDEN	8	5	.1	.4 (*)	.4	+ 50	12370.96	12371.58
and	9.9	2	.1	.5 (*)	.45	+ 46	12370.06	12370.63
SCHWARZ	19.6	2	.1	1.0 (*)	.7	+ 36	12370.96	12371.40
				Wt. average			12370.76	12371.33
BEARDEN,	10.2	1	.2	.5 (*)	.65	+ 64	12371.20	12371.99
JOHNSON	6.1	1	.2	.3 (*)	.55	+ 90	12370.75	12371.86
and WATTS	4.1 (+)	1	—	.2 (?)	.1	+ 24	12371.92	12372.22
				Average				12372.02
DUMOND, FELT and HARRIS	24.5	All	.2	6.0	3.4	+139	12370.02	12371.74
						Unweighted average of experiments		12371.70

(*) The spectrometer used in the Bearden experiments had a resolving power $\lambda/d\lambda \approx 10000$. Thus the half-width w is about 1 eV for 10 kV and is approximately proportional to the voltage. It is assumed that other factors contributing to effective half-width are negligible.

(+) This value was obtained by taking the difference between the 6.1 kV and 10.2 kV results; it therefore involves no error due to thermal energies. In the original report of the experiments it was considered less accurate than the other two determinations, but in the light of the various uncertainties cited it is now given the same weight as the others.

3·6. *Electron diffraction.* – The wave properties of the electron were first suggested by DE BROGLIE and soon afterwards confirmed in the experiment of DAVISSON and GERMER [107]. At non-relativistic velocities, the wave-length is h/mv. This may be determined by diffraction experiments; Bragg's Law applies just as in the case of X-rays [108]. However, since the specimens used are usually not single crystals but rather thin films formed by evaporation, the technique is similar to X-ray powder photographs. For a given Bragg angle θ, there will be some microcrystals oriented so that the beam of electrons strikes them at this angle of incidence. The contributions of various layers will then reinforce one another and strong direct reflection will take place; since the various microcrystals have random azimuth angles, the result will be a cone of rays making an angle of 2θ with the incident beam. For each Bragg plane there will be one cone corresponding to each order of the Bragg equation. Thus the wave-

length is obtained in terms of the measured angle and the grating space of the crystal, usually known in Siegbahn units.

The velocity of the incident electrons may be determined in two ways. The first is by means of direct measurement with the technique used by KIRCHNER [54] in his e/mc measurement. Such experiments have been performed by MEIBON and RUPP [109] and GNAU [110]. They yield essentially a value of $(h/m)(\lambda_s/\lambda_g)$; but the accuracy is not high, the error being of the order of .1%. The second method is to accelerate electrons by means of a known voltage V; in this case the non-relativistic energy is $10^8\,Ve/c$ and the corresponding velocity $v = (2\cdot 10^8\,Ve/mc)^{\frac{1}{2}}$. Combining this expression with the wave-length equation gives $(\lambda_s/\lambda_g)h/(em)^{\frac{1}{2}} = \lambda'(2\cdot 10^8\,V/c)^{\frac{1}{2}}$, where λ' is measured on the Siegbahn scale. When relativistic corrections to momentum and kinetic energy are included, this becomes

$$\frac{h}{(em)^{\frac{1}{2}}}(\lambda_s/\lambda_g) = \lambda'\left[\frac{V}{c}\left(2\cdot 10^8 + \frac{10^8\,Ve}{mc^3}\right)\right]^{\frac{1}{2}}.$$

The first precision determination of this type was made by VON FRIESEN [111].

A more accurate version of this experiment was recently performed by RYMER and WRIGHT [112]. They used a modified form of an electron microscope at 50 kV. The voltage was determined by a precision voltage divider, which was calibrated under full load. Four different substances were used to produce diffraction, viz., Al, NaCl, and CsI. The grating constant for NaCl [113] is taken from Bergen's [63] work. The constant for CsI (and possibly that for KCl which is based on unpublished work) is obtained from powder photographs and may be somewhat less accurate for this reason. The estimate of uncertainty in grating constants, 20 ppm, may perhaps be low; but the total error appears reasonable. It is stated in terms of standard deviation and corresponds to a probable error of about 67 ppm. Their result then becomes

$$\frac{h}{(em)^{\frac{1}{2}}}(\lambda_s/\lambda_g) = (.999\,54 \pm .000\,07)\cdot 10^{-8}\ \text{erg s/(esu g)}^{\frac{1}{2}} \qquad (70\ \text{ppm}).$$

3·7. *Compton effect.* – When a high energy photon is scattered by a free electron or by one lightly bound to an atom, the frequency of the scattered photon is less than that of the incident one. In the case of a free electron the theoretical explanation can be obtained by treating the photon as a particle with energy $h\nu$ and momentum $h\nu/c$ and using the principles of conservation of energy and conservation of momentum (see, for example, RICHTMEYER and KENNARD [114] or COMPTON and ALLISON [115]). The resulting change of wave-length is found to be $\Delta\lambda = (h/mc)(1 - \cos\varphi)$ where φ is the angle between incident and scattered radiation.

Actually, while atomic electrons behave almost as free particles for high frequency photons, some correction is required to take account of the binding forces. ROSS and KIRKPATRICK [116] developed a simplified theory indicating that this correction was proportional to the square of the wave-length for a given scattering material. They then performed an experiment using three different wave-lengths with carbon as scatterer. By extrapolating their results to zero wave-length they obtained $h/mc = (.024\,18 \pm .000\,04)$ Å. As far as can be determined from their paper and a recalculation of some of their data, wave-lengths were measured on the Siegbahn scale and the conversion factor λ_g/λ_s was not applied. If this is correct, the result should be expressed as

$$\frac{h}{mc}(\lambda_s/\lambda_g) = (2.418 \pm .004)\cdot 10^{-10}\ \text{cm} \qquad (1\,650\ \text{ppm}).$$

3·8. *Compton wave-length by annihilation radiation.* – When a radioactive substance emits a positron, the latter will eventually encounter an electron; both will then be annihilated with the emission of two photons. The probability of this process occurring is very small until the positron has slowed down to thermal velocity; hence the energy of the photons, i.e., $2h\nu$ must come almost entirely from the rest mass of the two particles, which is $2mc^2$. (The potential energy cancels out since the potential energies of the positive and negative particles must be equal and opposite when they collide). If λ_c' denotes the wave-length of the photons on the Siegbahn scale, the frequency ν is equal to $(c/\lambda_c')(\lambda_s/\lambda_g)$. Substituting this value for ν and equating the two energies yields

$$\frac{h}{mc}(\lambda_s/\lambda_g) = \lambda_c' .$$

This is known as the Compton wave-length, which was discussed in the previous section.

DuMond, Lind and Watson ([117] measured this wave-length by means of a curved crystal spectrometer and positrons emitted from a ^{64}Cu source. The value was slightly higher than the best indirect value; DuMond interpreted this as possible evidence for a difference between the mass of the electron and that of the positron, the latter being about 80 ppm lighter. Another measurement by Lind and Hedgran [118], comparing annihilation radiation with γ-rays emitted by ^{198}Au, seemed to confirm this view. However, DuMond further improved the accuracy of his spectrometer and discovered small mechanical nonlinearities which had affected his previous results. A newer measurement by Muller, Hoyt, Klein and DuMond [119] gave the value

$$\frac{h}{mc}(\lambda_s/\lambda_g) = (2.421\,3 \pm .000\,3)\cdot 10^{-10}\ \text{cm} \qquad (124\ \text{ppm}) .$$

They also recalculated the Lind and Hedgran result, based on their own measurements for ^{198}Au γ-rays, and found almost perfect agreement.

3·9. *Radiation constants.* – The spectral distribution of energy radiated by a black body was theoretically determined by Planck [120]. (See Richtmeyer and Kennard [121] for a good explanation of the theory, but note that most of the results are stated in terms of energy density rather than energy radiated by the body). The resulting equation is

$$J_\lambda = \frac{c_1}{\lambda^5(\exp[c_2/\lambda T] - 1)} ,$$

$$c_1 = 2\pi c^2 h , \qquad c_2 = ch/k ,$$

where λ is the wave-length, k is the Boltzmann constant, $J_\lambda \mathrm{d}\lambda$ is the energy radiated per unit area per unit time in the wave-length interval $\mathrm{d}\lambda$, and the other symbols have their usual meanings. c_1 and c_2 are known as the first and second radiation constants. By integration it is possible to derive the Stefan-Boltzman Law, which states that the total energy emitted by unit area per unit time is σT^4. Differentiation of J_λ gives Wien's displacement law, i.e., $\lambda_m T$ is a constant (where λ_m is the wave-length for which J_λ is a maximum). The values of these constants are thus shown to be

$$\sigma = (2\pi^5/15)(k^4/c^2h^3) ,$$

$$\lambda_m T = c_2/4.965\,11 = hc/4.965\,11\,k .$$

Various methods of measuring these constants have been described in a review by WENSEL [122] and more recently in a shorter paper by RUTGERS [123]. The constant σ may be measured by constructing a cavity to approximate a black body and measuring the total radiation at a known temperature with a thermocouple or bolometer. WENSEL lists 20 measurements and takes the unweighted mean; RUTGERS favors omitting the first four, which involve work previous to 1910. If this is done a more consistent set is obtained and the result is $\sigma = (5.74 \pm .02)\cdot 10^{-5}$ erg/cm^2 s °C^4, with the probable error computed by external consistency. Obviously the accuracy is extremely low as compared with other measurements of atomic constants.

The constant c_2 is determined principally by two methods: 1) The constant $\lambda_m T$ may be found and c_2 computed by the exact numerical relationship quoted above. WENSEL gives a table quoting seven values; the last five (those obtained since 1910) will be used in the present calculation, as in the Rutgers paper. 2) An optical pyrometer may be used to find the ratio of radiant energy flux at two different temperatures for a constant wave-length or at two different wave-lengths for a constant temperature. In this way the constant c_1 cancels out of the resulting equation and c_2 is obtained. A total of six such experiments by various workers are quoted by WENSEL and RUTGERS. The unweighted mean of these eleven values gives $c_2 = (1.434 \pm .001)$ cm °C. Undoubtedly a careful analysis and proper weighting would give a more accurate result, but the accuracy of the data does not seem to justify it. The value of c_2 has also been determined by RUTGERS [123] in photometric measurements giving the energy equivalent of luminous flux; the results are slightly lower than the mean quoted above.

In discussing these various results, both HOFFMAN [124] and DE GROOT [125] point out that they all depend on the accurate knowledge of the absolute temperature of the melting point of gold, which is used as a reference for high temperature work. This is now being redetermined carefully for the first time since 1911; MOSER [126] has reported his preliminary value is in essential agreement with the accepted figure. However, it seems best to allow for a possible error of at least 1 °C common to the above measurements. When the resulting error is then calculated, the above results become

$$\sigma = (5.74 \pm .03)\cdot 10^{-5} \text{ erg/cm}^2 \text{ s } ^\circ\text{C}^4 \qquad (5\,250 \text{ ppm}),$$

$$c_2 = (1.434 \pm .002) \text{ cm } ^\circ\text{C} \qquad (1\,400 \text{ ppm}).$$

3·10. *Index of refraction for X-rays.* – According to the theory of X-ray dispersion (see COMPTON and ALLISON [127] and WHEELER and BEARDEN [128]), the index of refraction μ of a material (or the decrement δ), defined as $\mu - 1$ can be computed by the equation

$$1 - \mu \equiv \delta = \frac{e^2 \lambda^2 N \varrho}{2\pi m c^2 M} \sum_s n_s (1 + A_s).$$

Here ϱ is the density of the material, M its molecular weight, λ the wave-length of the X-rays, n_s the effective number of electrons in the s^{th} level and A_s a factor which takes into account the electronic binding and the X-ray absorption for the s^{th} level. If the wave-length λ' is measured on the Siegbahn scale, the equation may be rearranged to give

$$\frac{Ne^2}{mc^2} (\lambda_s/\lambda_s)^2 = \frac{2\pi\delta M}{\lambda'^2 \varrho} \left[\sum n_s (1 + A_s)\right]^{-1}.$$

BEARDEN [129] employed this relation, together with the value of the faraday, to

obtain e/mc; he used a diamond prism since this crystal had low absorption and the factors n_s and n_g could be evaluated quite accurately. δ was measured for the Cu-K_β line and the density determined by placing the diamond in a special solution which could be adjusted so that the diamond would neither float nor sink. With the use of the wave-length on the Siegbahn scale quoted by BEARDEN [58], the result is $1.7056 \pm .0003$. BETHE and LONGMIRE [130] have pointed out that, when the scattering of X-rays by nucleii is included, the result is lowered by 2.7 parts in 10^4. The revised figure is thus

$$\frac{Ne^2}{mc^2}(\lambda_g/\lambda_s)^2 = (1.7052 \pm .0003)\cdot 10^{11}\ (\text{esu})^2/\text{erg mole} \quad (175\ \text{ppm}).$$

The principal source of error remaining may lie in the approximations used in the dispersion theory.

3·11. *Zeeman effect.* – The only spectroscopic measurement which can now be considered a determination of e/mc is that of the Zeeman effect. The energy levels of an atom in a magnetic field are shifted by an amount $Mg\mu_0 H$, where M is the magnetic quantum number, $\mu_0 = eh/4\pi mc$ is the Bohr magneton, and H is the magnetic field strength and g is the so-called Lande g-factor which is unity (or very nearly so) for atoms showing the normal Zeeman effect, i.e., having total spin zero. When the shift is expressed in wave numbers and when g is unity, the expression becmes $\Delta\tilde{\nu} = MHe/4\pi mc^2$. The selection rules for transitions require that $\Delta M = 0$ or ± 1, which means that in the normal Zeeman effect a single spectral line splits into three components in a magnetic field (see HERZBERG [131] for further details). By measuring the splitting and the field strength, it is thus possible to determine e/mc^2. Since c is known to high accuracy, it is possible to convert this to e/m or e/mc.

KINSLER and HOUSTON [132] determined such a value by measuring the Zeeman effect for Zn, Cd, He and Ne. All of these have singlet states and give the normal Zeeman effect. By observing the emitted light in the direction of the field, only two components were observed ($\Delta M = \pm 1$); these wave-lengths were measured by a Fabry-Perot interferometer. The mean of these measurements was given as $(1.7570 \pm .0007)\cdot 10^7$ emu/g. This error is the mean deviation, about twice the statistical probable error. However, it seems best to make some allowance for possible systematic error and to let the original figure stand. It is not entirely clear just what auxiliary constants were used, but it would appear that the result should be raised about 100 ppm to correct for a change in the conversion factor from international to absolute electrical units. The result then becomes

$$e/mc = (1.7572 \pm .0007)\cdot 10^7\ \text{emu/g} \quad (400\ \text{ppm}).$$

3·12.* *Rydberg constant and the atomic mass of electron.* – The Bohr theory gave energy levels (in wave numbers) for hydrogen and hydrogen-like atoms (e.g. He^+) as $Z^2R_\infty/n^2(1+m/m_n)$ where n is the principal quantum number, Z is the atomic number, $R_\infty = 2\pi^2me^4/ch^3$ is the Rydberg constant for infinite nuclear mass, and $1+(m/m_n)$, is a reduced mass correction factor depending on m/m_n, the ratio of the mass of the electron to that of the nucleus. Z and n, being integers, are precisely known; the energy levels can be determined to high accuracy by spectroscopic measurements of wave-length. If measurements

are available from two or more such spectra for atoms of known mass, it is possible to calculate both R_∞ and m. R_∞ can be determined to extremely high accuracy, while m will have a much higher error since it is determined by the difference between two quantities which are nearly equal. If the known masses are given in a.m.u., then the quantity directly determined is $M_e = Nm$, i.e., the atomic mass of the electron.

Actually, of course, the simple levels given by the Bohr theory do not exist. It has long been known that a given n level is split into levels corresponding to different j values. This effect is due to relativistic and spin corrections, and is given by the Dirac theory (see, for example, ROJANSKY [133]). Recently a further splitting has been discovered for levels with the same j, but different l. This is the so-called Lamb shift and consists principally of radiative corrections given by quantum electrodynamics. COHEN [134] has recently analyzed spectroscopic data on He, D, and H in the light of all these corrections and obtained for the Rydberg constant and the atomic mass of the electron

$$R_\infty = (109737.31 \pm .01)\ \text{cm}^{-1} \qquad (.1\ \text{ppm})$$

$$M_e = Nm = (54.895 \pm .008)\cdot 10^{-5}\ \text{amu} \qquad (145\ \text{ppm})\,.$$

(One figure has ben rounded off in R_∞). The error in R_∞ could be ten times as great as that stated and still not appreciably effect any of the constants to be derived from it. Thus it may be considered as precisely known when combined with other data. For this reason also, it turns out that the Lamb shift corrections to R_∞ have no appreciable effect on the derived constants; hence they will not be discussed in any detail in this section.

It should be noted that the measurement of $M_e = Nm$ mentioned above has frequently been referred to as a spectroscopic value of e/mc. It becomes so only when combined with the faraday $F = Ne/c$. Since there is considerable uncertainty as to the best value of F and since it is desirable to avoid correlations between various experiments so far as possible, it is here considered as a value of Nm.

3·13.* *Gyromagnetic ratio of the proton.* – The gyromagnetic ratio of the proton is defined as the ratio of its magnetic moment to its angular momentum. This is of interest in itself and is also valuable in furnishing a means of calibrating magnetic fields. It can be measured by determining the nuclear resonance frequency of the proton in a known field. The proton has spin $\hbar/2$, i.e., its projection in the direction of an external magnetic field is either $\hbar/2$ or $-\hbar/2$. The corresponding values of energy are $\pm \mu_p H$ where μ_p is the magnetic moment of the proton. The frequency ν_n of a transition between

these two states is easily found from the equation $h\nu_n = 2\mu_p H$ (ν_n is just the classical Larmor precession frequency). It follows that the gyromagnetic ratio γ_p is given by

$$\gamma_p = \frac{\mu_p}{\hbar/2} = \frac{2\pi\nu_n}{H}.$$

A good general survey of the theory and techniques of nuclear resonance has been given by PAKE [135]. Actually in experimental work the protons are not free particles, but are usually contained in samples of water or mineral oil. A small diamagnetic correction must then be made to account for shielding by the electrons. Since other experiments use a similar proton resonance device, it is convenient to make use of the directly measured quantities without diamagnetic correction, i.e., the apparent magnetic moment μ_p' and the apparent gyromagnetic ratio γ_p'.

This ratio has been measured very accurately by THOMAS, DRISCOLL, and HIPPLE [136] at the National Bureau of Standards. The proton sample was placed in a small inductance coil about 1 in. in diameter, which formed part of a resonant circuit fed by a 20 MHz oscillator. When the magnetic field was adjusted to produce proton resonance at 20 MHz, the nuclear absorption of energy lowered the Q and thus changed the voltage across the coil. The field strength was approximately 4700 gauss; it was produced by a large electromagnet with a 2 in. air gap about a foot in diameter. A pair of small Helmholtz coils immediately adjacent to the proton sample provided the fine adjustment to obtain resonance. The field of the electromagnet was measured by determining the force on a 10-turn rectangular coil carrying a known current. Almost all the force was on a 10 cm length on the lower end of the coil; but dimensions were measured very accurately and the necessary corrections made. The actual field was not quite uniform; it was carefully mapped by means of the proton resonance probe, which gave the ratio of the field at any point to that at a chosen reference position.

The error given is 22 ppm, which is intended as a limit of error. While numerous sources of error were considered, there were four principal ones, each estimated at 9 or 10 ppm, viz., precision of the balance, electrical standards, field distribution, and width of coil. The precision of the balance produces a statistical error; the last two errors may also be in part statistical. The statistical probable error is only 2 ppm. The error in the ampere has been previously discussed [137] and estimated at 6 ppm. Field distribution may be the most serious problem; relative field strengths are stated to at most five significant figures; therefore it would seem that the probable error due to this cause cannot be much less than 10 ppm. On the whole, it would thus seem that the figure of 22 ppm is fairly conservative, but that the probable error should be appreciably greater than 10 ppm. It will therefore be taken as

15 ppm and the result, without diamagnetic correction, stated as

$$\gamma_p' = 2\mu_p'/\hbar = (2.675\,23 \pm .000\,04)\cdot 10^4 \text{ s}^{-1} \text{ oersted}^{-1} \quad (15 \text{ ppm}) .$$

In regard to the diamagnetic correction, there are two points to be considered. The first question is how much the correction factor varies between different proton samples. GUTOWSKY and MCCLURE [138] found that the correction factor shift compared to H_2 gas as standard was $(.3 \pm .3)$ ppm for H_2O and $(3.7 \pm .3)$ ppm for mineral oil. THOMAS [139] obtained the values $-.6$ ppm and $+ 1.6$ ppm for water and oil respectively. A small amount of ferric salt was added to the water in the Thomas, Driscoll and Hipple experiment to reduce the relaxation time; this was compared with a standard oil sample used as a reference. Thus it is clear that the differences between various samples are small, a few ppm at most. The second problem is the absolute diamagnetic correction in H_2 gas; this is needed only in calculating the absolute values of the magnetic moment and gyromagnetic ratio. This correction has been calculated as $+ 26.8$ ppm by RAMSEY [140], $+ 26.6$ ppm by NEWELL [141], and $+ 29.5$ ppm (stated as an upper limit) by HYLLERAAS and SKAVLEM [142]. It seems reasonable to adopt the value of $+ 27$ ppm. With the inclusion of the Thomas correction between the standard sample and H_2, the final correction becomes approximately $+ 28$ ppm. This appears to be correct within about 1 ppm, which is completely negligible compared with the original experimental error. The corrected value now becomes

$$\gamma_p = (2.675\,30 \pm .000\,04)\cdot 10^4 \text{ s}^{-1} \text{ oersted}^{-1} \qquad (15 \text{ ppm}) .$$

3·14.* *Cyclotron resonance of the proton (proton magnetic moment in nuclear magnetons).* – A proton in a uniform magnetic field will revolve in a circle with angular velocity $\omega_c = He/m_p c$; this is known as the cyclotron resonance frequency of the proton. If the proton resonance frequency described in the last section ($\omega_n = 2\pi\nu_n = 4\pi\mu_p H/h$) is measured in the same field, the ratio is

$$\frac{\nu_n}{\nu_c} = \frac{4\pi m_p c \mu_p}{eh} = \frac{\mu_p}{eh/4\pi m_p c} = \frac{\mu_p}{\mu_n} .$$

This is the magnetic moment of the proton expressed in nuclear magnetons. The same diamagnetic correction is involved as before so that the directly measured frequency ratio involves μ_p' rather than μ_p.

SOMMER, THOMAS, and HIPPLE [143] at the National Bureau of Standards devised an ingenious experiment for measuring this ratio. The electromagnet was the same as that used in the THOMAS, DRISCOLL, and HIPPLE experiment, and the technique of measuring proton resonance was similar. The frequency ν_c was measured by means of a device called the « omegatron », which was somewhat like a small cyclotron and is shown in Fig. 9. It employed a uniform magnetic field, perpendicular to which was an electric field between two condenser plates. A gas pressure of 10^{-6} mm or less was maintained within the omegatron; protons or other positive ions were produced near the center by electron beam bombardment. A number of guard rings surrounded the ome-

gatron on four sides; these were given a positive d.c. potential (trapping voltage) of about .1 V to prevent protons from escaping in the axial direction, i.e., the direction of the magnetic field. The electric field was supplied by an oscillator with a frequency of approximately 7 MHz. When the frequency was the same as the cyclotron frequency ν_c, then any protons which started in proper phase were continuously accelerated since the direction of the field changed each time they completed half a revolution. (The principle is the same as that of the cyclotron except that the particles gain energy continuously rather than in discrete steps when crossing a gap.)

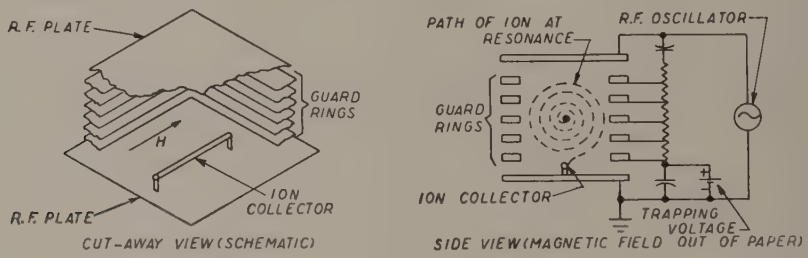


Fig. 9.

If the magnetic field was varied slightly, a proton might still gain energy from the field for a considerable number of revolutions, but would eventually become out of phase and decelerate. Thus, for any field strength such that the applied frequency was not quite equal to ν_c, there was a certain maximum radius attained by the protons. An electrode was located near one of the plates to collect the ions which reached this radius, about 1 cm. As the magnetic field was varied through the resonance value, a curve was obtained with half-width in the order of one part in 35000. A small correction to the measured ν_c was needed for the effect of space charge and trapping voltage. This was made by carrying out measurements on H^+, H_2^+, and D_2^+ and extrapolating to zero M, as indicated by a theoretical analysis. The theory was well supported by the consistency of the final results. The final value without diamagnetic correction was $\nu_n'/\nu_c = 2.792685$.

The error stated is 21 ppm. This includes an allowance of 5 ppm for statistical error (5 times the probable error) and the rest for possible systematic errors. The latter are believed to be due to three causes: (1) magnetic effect of the filament current, (2) magnetic shielding of the electrodes, and (3) asymmetry of the resonance peak. The first effect was checked by reversing filament current and the second investigated by placing the proton sample inside the omegatron. No definite change was observed in either case; such errors must have been in the order of 1 ppm or less. The unexplained asymmetry in the resonance peak amounted to a few ppm; it may have been in part statistical.

In light of these considerations it seems justified to divide the stated error by three and use 7 ppm. Thus the result becomes

$$\mu_p'/\mu_n = 2.79268_5 \pm .00002 \qquad (7 \text{ ppm})$$
$$\mu_p/\mu_n = 2.79276 \pm .00002 \qquad (7 \text{ ppm}) .$$

The same quantity has been measured by JEFFRIES [144], using an inverse or decelerating cyclotron, which is shown schematically in Fig. 10. A narrow beam of protons was accelerated to an energy of about 20 kV and injected into the cyclotron, which was 8.5 cm in diameter and was placed in a magnetic field of approximately 5 300 G. The cyclotron resonance frequency ν_c (ν_R in Jeffries's notation) was about 8 MHz for this field. When it was operated at precisely ν_c protons starting in the proper phase were decelerated each time they crossed the gap between the dees. For frequencies close to this, they could still be decelerated for many revolutions, but eventually became out of phase with the voltage and were accelerated again; this was the principal factor determining the band width of the observed resonance curve. If the cyclotron was operated at some odd multiple of ν_c, say $n\nu_c$, it was equally effective in decelerating the protons. However, for frequencies slightly off $n\nu_c$ the timing was more critical and the relative band-width reduced by $1/n$. In practice, most of the data were taken at the ninth harmonic. The frequency ν_n' was obtained by inserting a proton resonance probe in the same field, just as in the Sommer, Thomas and Hipple experiment.

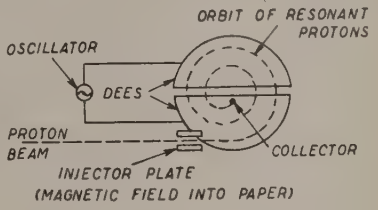


Fig. 10.

Experimental curves were obtained by varying the dee frequency ν through a small range around the resonant frequency $n\nu_c$; an approximate theory developed by Jeffries indicated that the curves thus obtained were *not* centered about the resonant frequency. The method of interpreting the results was essentially as follows. There existed a critical dee voltage V_c (about 200 V), below which no collector current could be obtained, since the protons had to lose a minimum amount of energy in the first revolution in order to clear the injector plate. At the voltage V_c only those protons whose phase was such that the decelerating voltage was a maximum as they crossed the gap could reach the collector. Jeffries's approximate theory showed that such protons would be defocused and strike the dees (i.e., move into or out of the paper in Fig. 10) if the dee frequency ν was slightly above the $n\nu_c$; for frequencies slightly below $n\nu_c$ focusing would occur. Hence the desired frequency $n\nu_c$ could be determined in principle by observing the high frequency cut-off of the curve when the dee voltage was equal to V_c. This was difficult to observe. Therefore curves were taken at a number of higher voltages and the results extrapolated to V_c by means of an approximate equation developed in the theory. The average obtained from many such determinations was a value of μ_p'/μ_n equal to 2.79237, which was rounded off to $2.7924 \pm .0002$.

JEFFRIES considered various sources of error; the above result includes estimated corrections for known systematic errors (except diamagnetic correction). However, the one error which overshadowed all others was that due to the approximate theory referred to above. He estimated that this error was not greater than one-third of the width of the resonance curve at the highest harmonic used, i.e., the 9th harmonic.

This gave an error of about 70 ppm, apparently intended as a limit of error. However, it seems safer to regard this figure as a probable error. The theory given by Jeffries was in excellent agreement with experiment for lower harmonics; however, for the 9th harmonic the band width predicted was in error by as much as a factor of three. He attributed this discrepancy to weak focusing action at higher frequencies. In extrapolating to V_c he used the observed band width rather than the calculated value in his theoretical equation. It is by no means certain that this one change is sufficient to make his equation a valid basis for extrapolation when the original theory has clearly broken down. Furthermore it seems very probable that, while an exact theory might place ν_c inside the resonance curve for $V = V_c$, it would not place ν_c totally outside this curve. Thus, if the extrapolation to cut-off voltage is carried out correctly, the residual error is more likely to be in one direction than the other.

Comparison of the JEFFRIES experiment with that of SOMMER, THOMAS and HIPPLE shows that (1) the theoretical error in the Jefiries experiment is much more difficult to assess quantitatively than the experimental ones in the STH work, (2) there is some reason to believe the Jeffries error is more likely to make the apparent value of ν_c too high than too low (which might explain the fact that his value is lower than the STH [143] result), and (3), if weighted inversely as the square of the errors as assigned above, the JEFFRIES result carries only about 1% of the weight of the STH one. Consequently, while the JEFFRIES result is very helpful in essentially confirming the STH value by a different method, it seems best to omit the former entirely in calculation of atomic constants.

3·15. *Cyclotron resonance of the electron (proton magnetic moment in Bohr magnetons).* – If the proton nuclear resonance frequency is compared to the cyclotron frequency of the electron ν_e, the ratio is the same as that derived in the preceding section with m_p replaced by m, i.e.,

$$\frac{\nu_n}{\nu_e} = \frac{\mu_p}{eh/4\pi mc} = \frac{\mu_p}{\mu_0}.$$

Hence the result is the magnetic moment of the proton expressed in Bohr magnetons.

This quantity was measured by GARDNER and PURCELL [145] in an experiment shown schematically in Fig. 11. A narrow ribbon of electrons was produced by an indirectly heated cathode and accelerated by a small voltage V_a. A uniform field of about 3 300 G was applied parallel to the beam. Due to small thermal velocity components perpendicular to the beam direction, the electrons moved in helical orbits with radii of the order of 3 μm. The rotational frequency, i.e., the cyclotron frequency, was approximately 9 400 MHz, the electrons completing roughly 1 000 revolutions between cathode and target. The magnetic field thus provided a focusing action and kept the beam from spreading appreciably between cathode and target under normal conditions. (It is interesting to compare this experiment with the BUSCH [87] method of determining e/mc).

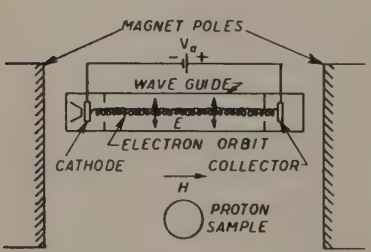


Fig. 11.

However, the section between cathode and target (about 2.3 cm long) was a part of a wave guide, which was excited so as to produce a high frequency electric field

perpendicular to the beam. When this frequency was equal to the cyclotron frequency of the electron, there was a gradual increase in the radius of the electron orbit, just as in the case of the omegatron described in the preceding section. Hence it was expected that a current minimum would be obtained in this case. Such a minimum was indeed observed when the accelerating voltage V_a was 5 V or greater. However, for values of V_a less than 3 V the current was found to be limited chiefly by space charge. In this case the high frequency field tended primarily to remove the slowest electrons from the center of the beam, thus decreasing space charge and actually increasing observed current. Since the width of this maximum was about one-tenth that of the minimum obtained for high values of V_a, the former was adopted as the more sensitive criterion. It was also found that the band width was substantially independent of high frequency power input provided this was kept below a certain maximum.

The proton resonance probe was placed in the field near the wave guide and the resonant frequency ν_n determined by substantially the same method described in previous sections. The absolute frequency was not needed; instead the 657-th harmonic of ν'_n was compared with ν_e and the difference was measured. A small error in the difference thus had a negligible effect on the result. The final value without diamagnetic correction was given as $\nu_e/\nu'_n = 657.475 \pm .008$.

Sources of error were carefully investigated. The filament current was reversed and the positions of proton probe and electron beam interchanged. These results were averaged for each run; the deviation from the average under various interchanges was about 50 ppm. The maximum variation of any run from the overall average was less than 10 ppm and the statistical probable error of the mean was about 2 ppm. Various sources of systematic error were investigated and found to be a few ppm at most. The error stated is 12 ppm and seems to be closer to a limit of error than a probable error. It thus appears safe to reduce this figure to 6 ppm and to state the final result, without diamagnetic correction, as

$$\mu_0/\mu'_p = 657.475 \pm .004 \quad (6 \text{ ppm}) .$$

4. – Quantumelectrodynamic experiments.

4·1.* *Theoretical considerations.* – The remaining experiments to be discussed are concerned with the microwave spectra of hydrogen and deuterium. Due to the well-known techniques of frequency demultiplication and comparison with a standard by means of beats, these measurements have a high inherent accuracy, which is of the order of 1 ppm. Consequently the necessary theoretical relations must be known to a corresponding accuracy in order to interpret the results properly. This requires the use of the recently developed theory of quantum electrodynamics to calculate a number of small but significant corrections. The experiments may then be regarded as fulfilling two different purposes: *a*) to provide a confirmation of the theory of quantum electrodynamics, and *b*) to furnish data for calculation of atomic constants. Fortunately there is enough data available to do both fairly satisfactorily.

Quantum electrodynamics has been treated in a comprehensive work by HEITLER [146]; CORBEN [147] and DYSON [148] have briefly described some of the basic concepts in

excellent qualitative discussions. It is impossible to do more than briefly outline a few points in the present report.

The theory began with DIRAC's [149] relativistic treatment of the electron. This equation succeeded in giving the spin and magnetic moment as results rather than requiring them as additional assumptions; it had the apparent drawback of requiring an infinite number of negative energy states. Dirac postulated that these levels were normally filled with an infinite sea of negative electrons, which usually had no observable consequences. However if sufficient energy were supplied, e.g., by a photon, an electron could be transferred from the negative levels with energy $E \leqslant -mc^2$ to a positive level with $E \geqslant mc^2$; the hole in the negative energy sea would then be recognized as a positively charged particle with the same mass as the electron. A few years later this prediction was verified with the discovery of the positron.

Positrons are observed experimentally only in processes involving energies of the order of 1 MeV or more. However in processes of much lower energy there may be so-called «virtual» electron-positron pairs. In a crude way these may be explained by saying that the uncertainty principle of quantum mechanics permits violations of the conservation of energy by an amount ΔE for a time Δt provided that $\Delta E \Delta t \sim \hbar$. These virtual pairs are not observed directly, but may have significant indirect effects on interpretation of measured quantities. Thus Dirac's theory of the electron is automatically a many particle theory. In some processes the possibility of virtual photons must also be taken into account; these processes result in what is termed vacuum polarization and the fluctuation of the vacuum field.

Vacuum polarization may perhaps be clarified by another approach. If an electron is surrounded by other ordinary electrons, they will of course be repelled. However, electrons in negative energy states may be considered as having negative mass; hence the same force which would repel an ordinary electron attracts those in the infinite negative sea. This effectively leaves a deficiency of electrons in the negative sea (i.e. a positive charge) at infinity. Hence the effective charge of the electron is increased by the vacuum polarization. In this process the total charge remains constant, which means that an additional electron near the original charge is always accompanied by a hole (i.e., a positron) at infinity. Such processes are known as second order processes; the corresponding terms in the various equations, which are of the order of α, are called second order corrections.

Unfortunately, it turns out that the effective charge thus computed for an electron together with its induced charges is always infinite, even in vacuum. This has been a major stumbling block in the theory. However, the experimentally observed charge must always include the effects of the vacuum. Hence the value of e originally inserted must be unobservable; the infinite expression calculated from it must be identified with the experimental value of e. This process is called charge renormalization. Similar infinities arise in the calculation of the effective mass and self energy of the electron. However, when both charge and mass are renormalized as described above, all these infinities may be removed, as shown by DYSON [150].

Significant effects occur when the same calculations are carried out in the presence of an electric or magnetic field. When these results are compared with the corresponding ones for vacuum, finite differences are obtained; these differences should be observable. For example, it is found that the field of a nucleus departs significantly from a Coulomb field due to vacuum polarization when the distance is of the order of the Compton wave-length (i.e. about 10^{-10} cm). Near the nucleus the potential energy of an electron is somewhat higher (less negative) than one would expect from Coulomb's law. The hydrogen-like wave functions [151] show that S electrons have a high probability of

being found near the nucleus, while for other states the probability is almost zero. Fig. 12 shows the energy levels for $n = 2$ in H, computed by LAMB and others on the basis of quantum electrodynamics; they are compared with the Dirac levels and with the still simpler prediction of the Bohr theory. The separation is called the Lamb shift; this will be discussed further in a subsequent section describing the measurement of the fine structure separation.

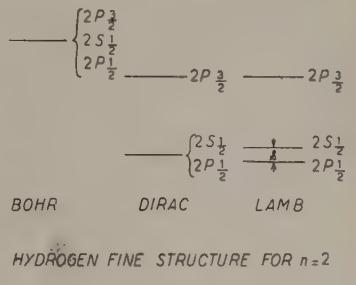


Fig. 12.

When an electron is placed in a magnetic field and quantum electrodynamic corrections to the energy are calculated, a term is obtained which is proportional to the projection of the spin along the field. It may be interpreted as a correction to the magnetic moment, which had previously been assumed to be exactly μ_0, as given by the Dirac treatment. This is now known as the anomalous magnetic moment of the electron. It is of course really a second anomaly; the first lies in the fact an that electron with spin $\hbar/2$ has a magnetic moment μ_0 instead of $\mu_0/2$, as would be expected on classical grounds. KARPLUS and KROLL [152] have calculated the necessary corrections through fourth order terms (i.e., terms in α^2) and obtained:

$$\mu_s = \mu_0 \left(1 + \frac{\alpha}{2\pi} - 2.973\,\frac{\alpha^2}{\pi^2}\right) = \mu_0\,(1.0011454)\,,$$

where α denotes the fine structure constant ($\alpha = 2\pi e^2/hc$). Additional terms are of order α^3 and higher; thus, if the theory is exact, the error should be less than 1 part in 10^8.

4·2.* *Anomalous moment of the electron.* – The anomalous moment of the electron has been experimentally measured to high accuracy; the theory is summarized by RAMSEY [153] and is basically similar to that of the Zeeman effect measurements [154]. If the proton had no magnetic moment, then the only magnetic moment in the ground state of H would be due to the electron spin. Thus there would be two degenerate levels in the absence of a field. A magnetic field would split these into two states with additional energies $2\mu_s H m_j$, where $m_j = \pm \frac{1}{2}$ depending on the orientation of the spin with respect to the field. This hypothetical situation is shown by the two dotted lines in Fig. 13.

In this case the Zeeman splitting of the two levels would correspond to a frequency $f = 2\mu_s H/h$. The field H might be measured in terms of the nuclear resonance frequency of the proton [155], as previously described, giving $H = h\nu_n/2\mu_p$. It would then follow that $\mu_s/\mu_p = f/\nu_n$.

Actually the situation is complicated by the magnetic moment of the

proton, which is responsible for the hyperfine structure. This introduces two additional energy terms. One is due to the interaction of the proton moment with the magnetic field of the electron, while the other is due to its interaction with the external magnetic field. In a field of a thousand gauss the former is of the same order of magnitude as the interaction of the electron moment with the external field, while the latter is smaller by a factor of about 10^3. Thus the second term, while not negligible, is of minor importance for fields normally used in experimental work.

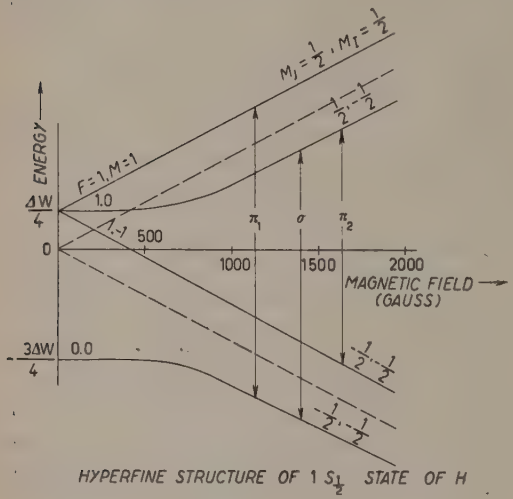


Fig. 13.

At zero field the only significant factor is the interaction of the proton moment with the electron field. When there is an orbital angular momentum of the electron, it is easy to see that when the total electronic angular momentum $\boldsymbol{J}$ is directed upward, the field at the nucleus is down; hence the position of highest energy occurs when $\boldsymbol{I}$, the spin angular momentum of the nucleus, is parallel to $\boldsymbol{J}$. When $\boldsymbol{J}$ consists only of spin angular momentum, i.e., in an S state, the simple classical treatment breaks down and the resulting expression becomes indeterminate (see RAMSEY [153]). However, a more accurate relativistic analysis, as given by HARGREAVES [256] and FERMI [257] indicates that the same conclusion holds. Thus, if $\boldsymbol{F} = \boldsymbol{I}+\boldsymbol{J}$ is the total angular momentum, the state $F = 1$ (spins parallel) has a higher energy than $F = 0$ (spins antiparallel), as indicated in Fig. 13. This difference ΔW corresponds to a frequency ν_H of about 1240 Hz. For low fields, in the order of 100 gauss or less, $\boldsymbol{I}$ and $\boldsymbol{J}$ may still be considered as coupled together to form a resultant $\boldsymbol{F}$, which precesses about the field H. Hence a Zeeman splitting is obtained, the $F = 0$ level remains unchanged, while the $F=1$ states split into three levels, corresponding to different values of M_F. For high fields. i.e., a few thousand gauss, the coupling between $\boldsymbol{I}$ and $\boldsymbol{J}$ breaks down and they precess independently about H. These two cases are indicated ni Fig. 14. The relevant quantum numbers for high fields are m_j and m_I.

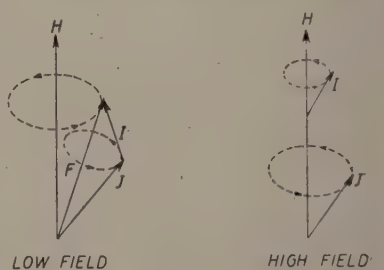


Fig. 14.

In this case the primary splitting is due to m_J; Fig. 13 shows that each pair of levels is split almost symmetrically and centered near the dotted line which would be obtained for zero proton moment; the level for which $\boldsymbol{I}$ and $\boldsymbol{J}$ are parallel is always slightly higher for fields under 10^5 gauss. The transition from the weak field to strong field case is analogous to that between the Zeeman and Paschen-Back regions in optical spectra.

The region of experimental interest is near this transition. This involves the solution of a secular determinant for almost degenerate states (the two levels for which $M_F = 0$) and has been carried out by BREIT and RABI [158]. Their result is

$$W(F, M_F) = -\frac{\Delta W}{4} - 2\mu_p H M_F \pm \frac{\Delta W}{2}\sqrt{1 + 2M_F x + x^2},$$

where the plus sign before the radical correspond to $F = 1$ and the minus sign to $F = 0$. The quantity x is defined by

$$x = \frac{2}{\Delta W}(\mu_J + \mu_p)H,$$

in which both μ_I and μ_p are taken as positive quantities. It will be noted that the levels (1, 1) and (1, -1) are linear functions of field throughout, just as in the low field approximation.

If the field H is measured in terms of the proton nuclear resonance frequency [155] ν_n (i.e., $H = h\nu_n/2\mu_p$) then $\mu_p H$ becomes $h\nu_n/2$ and $\mu_J H$ becomes $(h\nu_n/2)(\mu_J/\mu_p)$. Since $\Delta W = h\nu_H$, the energy equation in terms of frequency units may be expressed as

$$\nu(F, M_F) = -\frac{\nu_H}{4} - \nu_n M_F \pm \frac{\nu_H}{2}\sqrt{1 + 2M_F\left(\frac{\nu_n}{\nu_H}\right)\left(\frac{\mu_J}{\mu_p} + 1\right) + \left(\frac{\nu_n}{\nu_H}\right)^2\left(\frac{\mu_J}{\mu_p} + 1\right)^2}.$$

The observed frequencies can now be computed by taking differences between the appropriate levels; the transitions involved in the present experiments are those denoted by σ, π_1, and π_2 (in analogy with optical Zeeman effect terminology) in Fig. 13. If the frequency of one transition is measured along with ν_n (in the same field) and ν_H (without field), then clearly μ_J/μ_p may be calculated. Since proton resonance is observed in oil the directly determined quantity is actually μ_J/μ_p'. A small relativistic correction [159], giving a slight difference between the magnetic moment of the free electron and that bound in the H atom converts the result to μ_s/μ_p'.

KOENIG, PRODELL, and KUSCH [160] have measured the anomalous magnetic moment using the π_2 transition (1, $0 \leftrightarrow 1$, -1) indicated in Fig. 13. (The determination of ν_H will be discussed in the following section.) Their appa-

ratus is shown schematically in Fig. 15. The main electromagnet C produced a uniform magnetic field over a large area. The deflecting magnets A and B were of the two wire type (without iron core) and produced a strong inhomogeneous field over a small area. A beam of hydrogen atoms was obtained from a Wood's discharge tube at the left and collimated by a narrow slit. The atoms were deflected in one direction by the inhomogeneous field of A; this effect was normally just compensated by the field of B. Thus the beam was brought to a focus at the detector on the right; the position of the focus was essentially independent of velocity. The detector consisted of a Pirani gauge; this measures pressure by the electrical resistance of a wire, which changes due to the effect of convection on its temperature.

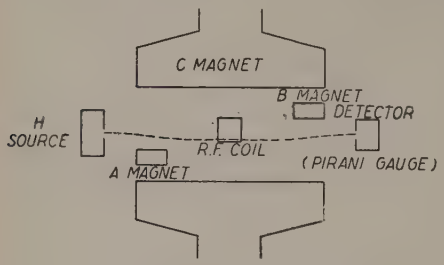


Fig. 15.

Transitions were obtained by applying a rf. field of 3655 MHz between the A and B magnets. This was furnished by a shielded, open-end rectangular box with small opening to admit the beam; it was fed by a coaxial line. When the field was adjusted to produce π_2 transitions at the applied radio frequency, this changed the direction of the magnetic moment of many atoms between the A and B magnets and a minimum was obtained at the detector. The proton resonance sample (not shown in the figure) was placed as near the beam as possible and allowance made for the gradient of the field. This correction as well as small relativistic and diamagnetic corrections appear to be the chief sources of systematic error. Their final result was $\mu_s/\mu_p' = 658.2288 \pm \pm .0006$, where μ_p' is stated for a spherical sample of mineral oil and the error is about twice the statistical probable error.

BERINGER and HEALD [161] measured the same quantity by microwave absorption technique, using both the π_1 and π_2 transitions (see Fig. 14). Atomic hydrogen was obtained from a Wood's discharge tube and passed axially in a fused silica tube through a microwave resonant cavity. The cavity resonated in the TE_{011} mode and was fed by a waveguide transverse to its axis. The waveguide continued on to a bolometer which measured the power transmitted through the cavity; this was, of course, greatly reduced when the radio frequency coincided with that of one of the hyperfine transitions. The radio frequency was fixed while the d.c. value of the magnetic field was varied. The field and the bolometer were both modulated at 30 Hz and the final signal obtained from a lock-in mixer; this technique greatly reduced background effects. One proton resonance unit was employed to maintain the d.c. level of the field

constant; a second was inserted in place of the resonant cavity and used to measure ν_n. Thus there was no problem about any spatial gradient of the field, but it was necessary to avoid or to average out time variations in the interval needed to replace the cavity by the proton probe. The final result (after corrections similar to those in the KOENIG, PRODELL and KUSCH experiment) gave $\mu_s'/\mu_p = 658.2298 \pm .0003$. However, the error represents only the statistical standard deviation and is obtained after rejecting 10 out of 14 runs (giving high values) as statistically improbable.

In view of the more conservative basis on which the KPK [160] error is stated, it seems reasonable to give equal weights to both measurements. The error of the mean will be taken as that given with the KPK result; this makes some allowance for any error in small correction factors common to both experiments. Thus the mean value is

$$\mu_s/\mu_p' = 658.2293 \pm .0006 \quad (1 \text{ ppm}) .$$

This value may be combined with that of the GARDNER and PURCELL experiment [162] and the result compared with the theoretical value [163] previously discussed. The experimental value thus obtained is $\mu_s/\mu_0 = 1.001147 \pm .000006$, while the theoretical value is $\mu_s/\mu_0 = 1.0011454$. This remarkably close agreement is strong evidence in favor of the essential correctness of the quantum electrodynamic calculations. Consequently the theoretical ratio of μ_s/μ_0 will henceforth be treated as an accurately known theoretical relationship. (This admittedly assumes a higher degree of accuracy than has been experimentally verified as yet.) Then, in view of the high accuracy of the anomalous moment experiment as compared with that of GARDNER and PURCELL, the latter will carry little weight in the final calculation of the constants, although it is of major importance in lending confidence to the recent theoretical developments.

4·3. *Hyperfine structure of hydrogen.* – The hyperfine splitting of the ground state of atomic hydrogen is the energy difference denoted by ΔW in Fig. 13. In frequency units this is equal to the quantity ν_H used in the last section. This is very nearly equal to the frequency of the σ transition $(1, 0 \leftrightarrow 0, 0)$ in a low field; they differ only by quadratic (and higher) terms in the field strength [164]. The frequency ν_H has been experimentally measured with high accuracy, but its theoretical interpretation is in some doubt.

NAFE and NELSON [165] determined ν_H by means of an atomic beam experiment; PRODELL and KUSCH [166] refined the method considerably, using essentially the same apparatus as in the KOENIG, PRODELL and KUSCH experiment described above and shown in Fig. 15. The chief difference was in the removal of the C magnet, only the residual laboratory field being used. An open loop of vertical copper plates shorted below the beam was employed and oriented to produce both π and σ transitions. The π_1 and π_2 lines were measured with lesser precision and used to make a small quadratic field correction to the σ line; this amounted to about 1 ppm. The result of this experiment

then gave $\nu_H = (1\,420.405\,1 \pm .000\,2)\ s^{-1}$, where the probable error (14 ppm) is purely a statistical one. It should be noted that the full width of the resonance curve at half maximum was about 33 kHz; the ratio of this to ν_H is 23 ppm. PRODELL and KUSCH point out that it would be difficult to prove the absence of asymmetry in the resonance curve sufficiently to justify confidence in the statistical error. However, they did succeed in eliminating certain experimental causes of asymmetry by taking data over a wide range of rf. power input.

WITKE and DICKE [167] determined ν_H by means of microwave absorption technique similar to that used by BERINGER and HEALD in measuring μ_s/μ_p'. They used a cylindrical resonant cavity excited in the TE_{112} mode with the sample in a glass container at the center. The atomic hydrogen was produced by a Wood's discharge tube and mixed with molecular hydrogen to prevent it from diffusing to the walls too rapidly and then recombining. A series of runs were taken at three pressures and then extrapolated to zero pressure. The magnetic field strength was only .06 G; this was oriented parallel to the magnetic field of the rf. so as to produce only σ transitions. The experiment gave $\nu_H = (1\,420.405\,80 \pm .000\,05)\cdot 10^6\ s^{-1}$, where the error is again only a statistical one.

The small but significant disagreement between these results may be due to the possible asymmetry discussed above. It therefore appears best to take the mean of these values and estimate the probable error conservatively on the basis of external consistency; the result is

$$\nu_H = (1\,420.405\,5 \pm .000\,3)\cdot 10^6\ s^{-1} \qquad (.2\ \text{ppm})\,.$$

The theoretical interpretation begins with the equation derived by FERMI [153, 157]. This may be qualitatively understood as follows. The hyperfine separation is due to the interaction of the nuclear moment with the field of the electron, which in an S state is due only to its spin. The field of a dipole falls off as r^3; hence the interaction energy should be proportional to $\mu_p\mu_s/(r^3)_{av}$. As previously mentioned, the actual expression is indeterminate unless treated relativistically; however, $(r^3)_{av}$ may be expected to be proportional to the cube of the Bohr radius a_0. It follows that

$$\Delta W \sim \left(\frac{\mu_p}{\mu_0}\right)\frac{\mu_0^2}{a_0^3} = \left(\frac{\mu_p}{\mu_0}\right)\left(\frac{he}{4\pi mc}\right)^2\left(\frac{4\pi^2 me^2}{h^2}\right)^3 = \frac{hcR_\infty}{2}\left(\frac{\mu_p}{\mu_0}\right)\alpha^2\,.$$

The detailed Fermi calculation gave a numerical factor of 16/3 rather than $\frac{1}{2}$.

This expression is in turn modified by several small corrections. Three of these are relatively straightforward: (1) BREIT [168] obtained a correction factor of $3\alpha^2/2$ by refining the mathematical approximations used in Fermi's relativistic treatment. (2) BREIT and MEYEROTT [169] showed an additional correction was necessary because of the motion of the nucleus. This is approximately equivalent to replacing m by the reduced mass in the expression for the Bohr radius; thus the correction is very nearly $(-3m/m_p)$. (3) When the anomalous moment of the electron is considered, the product $\mu_p\mu_s$ is equal $(\mu_p/\mu_s)(\mu_s/\mu_0)^2\mu_0^2$, thus involving the square of the theoretical expression [163] for μ_s/μ_0. BETHE and LONGMIRE [130] pointed out that two additional corrections are needed for a more exact treatment; i.e., allowance for distributed nature of the proton and electron magnetic moments rather than treating them as point dipoles. The electron moment extends over the order of a Compton wave-length; this effect can be calculated by a relativistic quantum electrodynamic treatment of the two particle problem; a small additional reduced mass correction is also obtained. How-

ever, the effect of the proton moment poses a more serious problem. While the electron moment is very nearly one Bohr magneton, the proton moment is almost 2.8 nuclear magnetons. This anomalously high value is presumably due to its interaction with the meson field; unfortunately there is no generally accepted meson theory by which the necessary calculations may be made.

KARPLUS and KLEIN [170] and KROLL and POLLOCK [171] computed the second-order radiative corrections, which include the distributed nature of the electron dipole. Their calculations were in close agreement. The Kroll and Pollock result (with the correction of a typographical error in sign) was

$$\nu_H = \frac{16\alpha^2}{3} cR_\infty \left(1 + \frac{3\alpha^2}{2}\right)\left(\frac{m_r}{m}\right)^3 \left(1 + \frac{\alpha}{2\pi} - \frac{2.97_3\alpha^2}{\pi^2}\right) \cdot$$

$$\cdot \left(\frac{\mu_p}{\mu_s}\right)\left[1 + \frac{\alpha}{2\pi} - \frac{2.973\alpha^2}{\pi^2} - \alpha^2\left(\frac{5}{2} - \ln 2\right)\right] P_r P_s ,$$

where $m_r = m(1 - m/m_p)$ is the reduced mass. The first and second terms in parentheses are Breit's relativistic correction and the approximate reduced mass correction. The next two terms together give the proton moment in terms of the Bohr magneton. The bracket gives the electron moment in terms of the Bohr magneton plus additional radiative corrections. P_r and P_s are addition terms, then uncalculated, due to proton recoil and to the distributed nature of the proton moment. Using this equation, KROLL and POLLOCK obtained $\alpha^{-1} = 137.03651 \pm .00028$, if P_r and P_s are set equal to unity.

Further work has been carried out by ARNOWITT [172] and by NEWCOMB and SALPETER [173]. Their procedure essentially consists of dividing the proton magnetic moment into two parts — a Dirac moment which arises naturally from a relativistic treatment of the proton and a Pauli type moment which is added to bring the total up to the experimentally observed value. Their results contain a logarithmic divergence, which can be removed only by introducing a cut-off corresponding to the Compton wave-length of the proton or meson. ARNOWITT states that the result is insensitive to which one is used. NEWCOMB and SALPETER indicate that the difference is significant; they conclude that this crude non-relativistic spreading of the nucleon bears little relation to reality. Consequently the theoretical situation still appears unsatisfactory.

An indication of this difficulty is found in the discrepancy between the theoretical and experimental ratios of the hyperfine splitting in hydrogen and deuterium, i.e. ν_H/ν_D. PRODELL and KUSCH [166] point out that this difference is 170 ppm. Of course, this may be largely due to the more complicated structure of the deuteron.

If the Kroll and Pollock result is corrected for the present values of the auxiliary constants (including a diamagnetic correction [155] of 29 ppm) without adding any new correction terms, the result is $\alpha^{-1} = 137.0369$. It is difficult to estimate the probable error properly. The principal experimental errors are in c, (μ_p/μ_s), and the diamagnetic correction, each being of the order of 1 ppm. However, the uncertain terms related to proton structure were originally estimated by BETHE and LONGMIRE [130] to be of the order of 16 ppm; SALPETER [174] predicted that they might be more than 20 ppm. (There is now some indication [173] that certain terms may be fortuitously small). Furthermore, terms in α^3 have not been calculated for any corrections. Consequently it seems unsafe to put the probable error at less than 10 ppm in ν_H or

5 ppm in α^{-1}. Hence.

$$\alpha^{-1} = \frac{hc}{2\pi e^2} = 137.0369 \pm .0007 \qquad (5 \text{ ppm}),$$

where the error is given on a rather questionable basis.

It should be remarked that the above uncertainties do not affect the use of ν_H in the anomalous moment experiments. These require only the experimental quantity ν_H, not its interpretation in terms of α.

4·4.* *Fine Structure Separation.* – The fine structure constant α was originally determined by interferometric measurement of the fine structure separation of optical spectra [175]. BIRGE [176] pointed out that α could be obtained with higher accuracy from the $L^{II}L^{III}$ separation of X-ray lines; he calculated a value of $\alpha^{-1} = 136.95 \pm .05$ with the aid of a theoretical analysis by CHRISTY and KELLER [177]. BETHE and LONGMIRE [130] later noted that this value should be raised to 137.11 due to the anomalous moment of the electron.

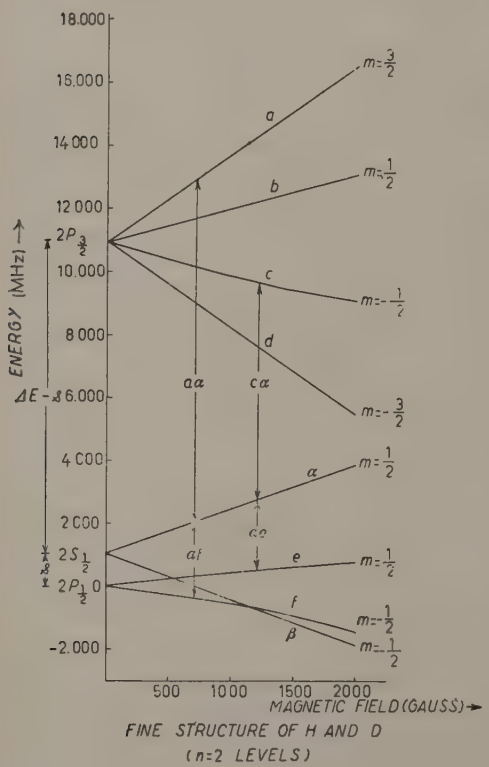


Fig. 16.

A great increase in accuracy can be attained by using microwave techniques. This makes it possible to measure directly the energy difference between two states of almost equal energy rather than compute it from the small difference between two frequencies almost equal in magnitude. An extensive and painstaking investigation of the fine structure of the first excited state of H and D has recently been completed at Columbia University. The earlier work, including most of the theoretical calculations, was carried out by LAMB and RETHERFORD [178], while the final experimental results needed in the present report were obtained by TRIEBWASSER, DAYHOFF, and LAMB [179, 180].

The quantity of primary interest is the separation ΔE between the $2P_{\frac{3}{2}}$ and $2P_{\frac{1}{2}}$ levels (see Fig. 16). A direct transition between these states is prohibited by the selection rule $\Delta l = \pm 1$. Hence ΔE can best be determined

by two measurements, the separation $\mathcal{S}$ between the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ levels and the separation $\Delta E - \mathcal{S}$ between the $2P_{\frac{3}{2}}$ and $2S_{\frac{1}{2}}$ levels. It should be emphasized that the $2S_{\frac{1}{2}}$ level is only a convenient stepping stone to go from $2P_{\frac{3}{2}}$ to $2P_{\frac{1}{2}}$. Any other level to which transitions from these states are permitted would do as well in principle, although the precision might be much less. Thus any uncertainties in the theoretical interpretation of the Lamb shift $\mathcal{S}$ have no bearing on the experimental accuracy of measuring ΔE.

These separations were actually computed from measurements in moderately high magnetic field. One reason was the large half-widths of the microwave lines. It was convenient to maintain a constant rf. power input of fixed frequency and to observe the resonance curve by changing the magnetic field. For this reason it is necessary to discuss the Zeeman splitting of the fine structure of hydrogen.

Fig. 16 shows the energies as functions of field for the $n = 2$ state of H or D (which are almost identical). The notation designating different levels is the same as in the TRIEBWASSER, DAYHOFF and LAMB work. Lamb's [181] results for the various energy levels, in terms of frequency units, may be rewritten as:

For $2P_{\frac{3}{2}}$, $m = \pm \frac{3}{2}$ (a and d levels),

$$\nu_{a,d} = \frac{\Delta E}{h} \pm \left(g_L + \frac{g_s}{2}\right)\left(\frac{\mu_0 H}{h}\right).$$

For $2P_{\frac{3}{2}}$, $m = \pm \frac{1}{2}$ (b and c levels),

$$\nu_{b,c} = \frac{\Delta E}{h} + \left[\pm\left(\frac{g_L}{3} + \frac{g_s}{6}\right) + \frac{2}{9}(g_s - g_L)^2\left(\frac{\mu_0 H}{\Delta E}\right)\right]\left(\frac{\mu_0 H}{h}\right) + \cdots.$$

For $2P_{\frac{1}{2}}$, $m = \pm \frac{1}{2}$ (e and f levels),

$$\nu_{e,f} = \left[\pm\left(\frac{2g_L}{3} - \frac{g_s}{6}\right) - \frac{2}{9}(g_s - g_L)^2\left(\frac{\mu_0 H}{\Delta E}\right)\right]\left(\frac{\mu_0 H}{h}\right) + \cdots.$$

For $2S_{\frac{1}{2}}$, $m = \pm \frac{1}{2}$ (α and β levels),

$$\nu_{\alpha,\beta} = \frac{\mathcal{S}}{h} \pm \frac{g_s \mu_0 H}{2},$$

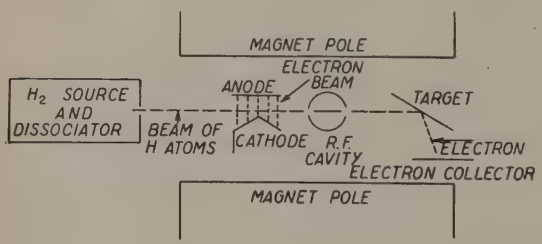
where the plus or minus sign refers to the first or second subscript respectively. The exact form of the equations for $\nu_{e,f}$ and $\nu_{b,c}$ was given and used by Lamb. However, they are expressed here in Taylor series expansions through quadratic powers of H; this form is more instructive in showing the dependence of the levels on the different variables. The factor $g_s = 2\mu_s/\mu_0$ is given theoretically [163]; the effective $g_L = 1 - (m/m_p)$, which includes a reduced mass correction, is known to very high accuracy.

The a, d, α and β levels are linear functions of $(\mu_0 H/h)$ and have an obvious physical interpretation; the slopes are approximately ± 2 and ± 1 respectively. The b, c, e and f levels are almost linear functions of $(\mu_0 H/h)$ with respective slopes of $\pm \frac{2}{3}$ and

$\pm \frac{1}{2}$; however, they also contain quadratic terms in H involving the ratio $(\mu_0 H/\Delta E)$. For the fields employed in the experiment the quadratic term was always less than 10% of the total field correction. Hence it was easily possible to assume a value of ΔE in the quadratic terms, calculate ΔE from the measured frequencies (e.g., $a\alpha$ and αf) and fields, and refine the result by successive approximations if necessary.

It should be noted that the hyperfine structure has been ignored in the above discussion. Hence the lines in Fig. 16 really correspond to the dotted lines of Fig. 13. However, the hyperfine splitting is much smaller than in the ground state due to the increase in average electron radius; the S state is split by 88 MHz and the P state by only 29 MHz. The line widths of the observed transitions are such that the hyperfine splitting is barely resolved, if at all.

The experimental apparatus is shown schematically in Fig. 17. An oven, which dissociated about two-third of the H_2 molecules, was used as a source of atomic hydrogen (or deuterium.) A collimated beam of atoms passed into a magnetic field; here it was bombarded by a transverse beam of electrons accelerated by a grid (not shown) at roughly 13.5 V. As a result a small fraction (of the order of 1 in 10^7) of the atoms was excited by collision to the $2S_{\frac{1}{2}}$ state, which is metastable. Its exact lifetime is strongly dependent on perturbing electric fields, but can be made much greater than that of the P states. Since under operating conditions the magnetic field was fairly close to the βe cross over point (574 G), most of the β component was removed through transitions to the e level; a small d.c. electric field in the rf. cavity furnished sufficient perturbation to make this practically complete. The beam then passed on to a tungsten plate, which acted as a metastable detector. In losing their excitation energy by collision, many of the metastable atoms were able to eject electrons from this surface. These were collected by a second electrode and the resulting current measured.



FINE STRUCTURE EXPERIMENT

Fig. 17.

If transitions from a $2S$ to $2P$ level were induced in the beam by an rf field, the atoms would then go quickly to the $1S$ ground state by spontaneous emission. This resulted in a lower current output of the metastable detector. At resonance peaks, about 30% of the metastable α component was « quenched » in this way. Two different rf cavities of appropriate design were used, depending on whether the desired transition required $\Delta m = 0$ or $\Delta m = \pm 1$ (σ or π transition). Both were fed by a coaxial line from an oscillator with carefully controlled frequency and power level. Resonance curves were ob-

tained by scanning the magnetic field through the region of interest. In some cases the resulting curves were as wide as 100 MHz at half maximum. Since it was desired to obtain a result good to .1 MHz, all known causes of asymmetry were carefully investigated and corrections made wherever significant.

The magnetic field was measured by means of a search coil and bridge circuit. For all runs used in final calculations, this was calibrated by means of a proton resonance probe. The calculation of the field corrections [180, 181] is rather complicated to follow; it appears to be equivalent to taking μ_0/h from BW [17] constants and measuring the field in terms of the THOMAS, DRISCOLL, and HIPPLE [136, 155] experiment. Since the field corrections total almost 20% of the value of ΔE, the error due to this correction and the correlation with other experiments should not be overlooked. This point was noted in the recent BEMT [2] evaluation; it was tentatively concluded that the additional error and the correlation were not too serious.

A closer study shows that this argument can now be put on a much firmer basis. Calibrating the field in terms of the TDH [136] experiment meant essentially computing H from

$$H = \left(\frac{h}{2\mu_p}\right)_{\text{TDH}} \nu_n = 2\pi \left(\frac{1}{\gamma_p}\right)_{\text{TDH}} \nu_n ,$$

where ν_n was the measured quantity and γ_p was the TDH value. The field correction in frequency units thus employed

$$\frac{\mu_0 H}{h} = 2\pi \left(\frac{\mu_0}{h}\right)_{\text{BW}} \left(\frac{1}{\gamma_p}\right)_{\text{TDH}} \nu_n .$$

On the other hand, this quantity could be now computed as follows:

$$\frac{\mu_0 H}{h} = \frac{\mu_0}{h}\left(\frac{h\nu_n}{2\mu_p}\right) = \frac{1}{2}\left(\frac{\mu_0}{\mu_p}\right) \nu_n .$$

The ratio (μ_0/μ_p) is known to about 1 ppm from the experimental measurements [164] of (μ_s/μ_p) and the theoretical relation [163] giving (μ_s/μ_0). This value of (μ_0/μ_p) should be accurate to about 1 ppm, while the TDH experiment and the BEARDEN and WATTS [17] constants involve errors many times as great.

However, the two methods will give the same results if it happens that the factor $2\pi(\mu_0/h)_{\text{BW}}(1/\gamma_p)_{\text{TDH}}$ used in the actual experiment equals the factor $(\mu_0/2\mu_p)$ appearing in the second equation. These values are 328.7375 and 328.7381 respectively, i.e., the difference is less than 2 ppm. Since the entire correction is about 20% of ΔE, this difference amounts to about .4 ppm in ΔE, which is negligible. Thus any correlation between this experiment ando ther data may safely be ignored. Furthermore, even if the TDH value should be

substantially altered, it will not be necessary to revise the value of ΔE as long as (μ_0/μ_p) does not change appreciably.

The Lamb shift $\mathcal{S}$ for H and D has been measured by TRIEBWASSER, DAYHOFF, and LAMB [179]. They use αe and αf transitions at 1160 gauss and 700 gauss respectively (2195 and 2395 MHz), as shown in Fig. 17. The mean of these two values for deuterium is 1059.00 MHz with a statistical probable error of .03 MHz based on internal consistency of the two measurements. Actually each result differed from the mean by about .05 MHz, which gives a very reasonable statistical picture. In the case of H, where asymmetry corrections for the two transitions differed by 2 MHz, the close agreement between the resulting values of $\mathcal{S}$ gave strong evidence for the validity of the corrections. (The corrections for D were smaller and almost equal.) The field measurements have already been discussed; there is no other obvious source of systematic error. The experimenters multiplied the average deviation of the mean by three to obtain a limit of error of .1 MHz. They gave no specific estimate of systematic error here, although in the experiment to be discussed below, they allowed .05 MHz, intended as a limit of error. On the basis of all this it seems reasonable to adopt a probable error of .05 MHz for the $\mathcal{S}$ measurement.

It may be noted in passing that the experimental value of $\mathcal{S}$ differed from the theoretical result given by SALPETER [182] by about .5 MHz. While this discrepancy poses an important problem, the agreement may still be regarded as a major achievement of quantum electrodynamics. It should be emphasized that the entire Lamb shift, not merely some small corrections to it, is due to quantum electrodynamic effects. As already noted, this discrepancy is of no real concern in the fine structure measurement unless it is taken to mean that the experimental value of $\mathcal{S}$ is in error.

DAHYOFF, TRIEBWASSER, and LAMB [180] measured $\Delta E - \mathcal{S}$ using the $a\alpha$ and $c\alpha$ transitions at 630 and 1190 gauss respectively (10795 and 7195 MHz). They rejected the αc measurements from the final result; these were based on a method of field calibration using an $\alpha\beta$ transition, which was proved to be less dependable than the proton resonance technique. (The difference between the $a\alpha$ and $c\alpha$ results was .2 MHz.) They obtained a limit of error by adding 3 times the probable error (.017 MHz) to an estimated possible systematic error of .05 MHz. A probable error of .05 MHz will be used here. Adding the results of the two experiments and combining probable errors in the usual way gives

$$\nu_{\Delta E} = \frac{\Delta E}{h} = (10\,971.58 \pm .07)\ \text{MHz} \qquad (6\ \text{ppm}).$$

It is now necessary to use this value in a theoretical relation to calculate α. The order of magnitude may be quickly obtained by recalling that this is an interaction between the spin moment of the electron and the magnetic field

created by the motion of the proton as seen from the electron; the separation will be of the order of the Bohr radius a_0. Hence the energy should be of the order of μ_0^2/a_0^3; this is roughly the same as the estimate for the hyperfine splitting with the omission of the factor (μ_p/μ_s). The necessary calculations are summarized by LAMB [183] and the result stated in the fine structure experiment [180]. It may be rewritten as

$$\alpha^{-1} = \left[\frac{cR_D}{16\nu_{\Delta E}}\left(1 + \frac{5}{8}\alpha^2 + \frac{\alpha}{\pi} - \frac{5.946}{\pi^2}\alpha^2\right)\right]^{\frac{1}{2}},$$

where $\nu_{\Delta E}$ is the frequency corresponding to ΔE. The first two terms come from the Dirac treatment [149], while the last two are based on the second and fourth order anomalous moment corrections. The equation may, of course, be solved by successive approximations. Correcting Dayhoff's figure for the values of c and R_∞ adopted in the present report gives.

$$\alpha^{-1} = \frac{hc}{2\pi e^2} = 137.037\,1 \pm .000\,4 \qquad (3 \text{ ppm}) .$$

The above equation is exact, so far as is known, except for higher order terms in α. Hence, unless these are unexpectedly large, there should be no theoretical uncertainty in the value.

C) Analysis

1. – General principles.

The experiments just discussed represent a rather formidable mass of data. It is fairly obvious that experiments with errors much greater then 100 ppm, will carry negligible weight in the final adjustment. However, it seems desirable to adopt some criterion for accepting or rejecting borderline data.

The relative error by itself is not an infallible standard. For example, the RYMER and WRIGHT determination of $h/(em)^{\frac{1}{2}}$ has been assigned a probable error of 70 ppm. It could equally well have been listed as a determination of h^2/em. In this case, the error would be doubled, but the significance of the data would be unchanged.

Consequently the following procedure will be adopted: The constants will first be calculated by a direct solution (i.e., one which is not overdetermined) of the most precise experimental data. (A unique choice of such data will not always be possible, of course.) This experimental data will be referred to as the « trial data ». From the trial data it is also possible to calculate any

desired combination of constants with the corresponding probable error. The error of any other experiment may thus be compared with that obtained from the trial data. This will be illustrated by an example later on.

At this point it should be noted that the probable error of an experiment is never known exactly. For example, it was shown by GAUSS [184] that on a purely statistical basis the relative probable error of a probable error is $.48/\sqrt{n}$, where n is the number of observations. Thus with 25 observations the probable error itself may have an uncertainty of about 10%. In the experiments considered here, the statistical probable errors are subject to this order of uncertainty; the systematic errors are generally much more difficult to evaluate. Since data will be weighted as the square of the probable error in the final adjustment, the weighting is subject to an uncertainty of at least 20%.

This discussion shows the fallacy of including data of low weight. If one experiment has three times the probable error of another, it will carry only about 11% as much weight. However, the weight of the second experiment is uncertain by more than this amount. Hence, as a rule of thumb, it seems pointless to include any experiment when its error is more than three times that of any other combination of experiments yielding the same result. There might be an exception if a great quantity of additional data where available, with each item having an error barely too high to meet the above criterion.

By the same token when some items used in the adjustment have errors much smaller than the others, it is pointless to treat such quantities as variables for adjustment. These quantities may be then termed auxiliary constants; the value and error of each one is fixed by a single type of experiment. This procedure assumes that such constants do not overdetermine any variable or appear to too high a power in any calculation.

2. – Selection of input data.

Table VI summarizes all of the experimental results with errors of 100 ppm or less (as well as the theoretical relation for μ_s/μ_0); the left hand column indicates the experiment involved and the section of Part B in which it is described. The first group comprising five relations all involve errors of 1 ppm or less; they do not overdetermine any of the unknowns. Clearly they may be treated as auxiliary constants; in fact they have already been so used in many of the other equations.

A direct solution is possible with the first two groups of equations. With the help of the auxiliary constants, Eqs. (6), (7), and (8) can be rewritten in terms of N, e and h. Obviously c may be eliminated wherever it appears by Eq. (4); m may be similarly treated by Eq. (2). Through the use of Eqs. (1)

TABLE VI. – *Summary of experimental data.*

Note. - All values are in c.g.s. units. e is given in e.s.u. and magnetic moments in erg/Oe.

Experiment (Section Ref. Part B)	Quantity measured	Result	Error (ppm)	Eq. No.
Theoretical anomalous moment of electron (4·1)	μ_s/μ_0	$= 1.001\,145\,4$	0	(1)
Rydberg constant (3·12)	$R_\infty = 2\pi^2 me^4/ch^3$	$= 109\,737.31$	.1	(2)
Exp. anomalous moment of electron (4·2)	μ_s/μ_p'	$= 658.229\,3$	1	(3)
Velocity of light (2·1)	c	$= 2.997\,928 \cdot 10^{10}$	1	(4)
Mass of proton (2·8)	M_p	$= 1.007\,595\,7$	1	(5)
Fine structure separation of D (4·4)	$\alpha^{-1} = hc/2\pi e^2$	$= 137.037\,1$	3	(6)
Cyclotron resonance of proton (3·14)	μ_p'/μ_n	$= 2.792\,685$	7	(7)
Gyromagnetic ratio of proton (3·13)	$2\mu_p'/\hbar$	$= 2.675\,23 \cdot 10^4$	15	(8)
Electrochemical faraday (2·3)	$F = Ne/c$	$= 9\,651.4$	30	(9)
Avogadro's number (X-ray Cryst. Dens.) (2·6)	$N' = (\lambda_g/\lambda_s)^3 N$	$= 6.061\,4 \cdot 10^{23}$	33	(10)
Ruled X-ray gratings (2·7)	λ_g/λ_s	$= 1.002\,02$	20	(11)
Gas constant (2·9)	R	$= 8.317\,0 \cdot 10^7$	12	(12)
Cyclotron resonance of electron (3·15)	μ_0/μ_p'	$= 657.475$	6	(13)
Hyperfine structure of H (4·3)	$\alpha^{-1} = hc/2\pi e^2$	$= 137.036\,9$	5	(14)
X-ray high freq. limit (3·5)	$(h/e)(\lambda_s/\lambda_g)$	$= 1.376\,53 \cdot 10^{-17}$	65	(15)
Electron diffraction (3·6)	$[h/(em)^{\frac{1}{2}}](\lambda_s/\lambda_g)$	$= .999\,54 \cdot 10^{-8}$	70	(16)

and (3), μ_p' is expressible in terms of μ_0, which in turn is defined as $eh/4\pi mc$. Since, by definition, the nuclear magneton $\mu_n = \mu_0(m/m_p)$ and $M_p = Nm_p$, Eq. (7) may be treated as follows:

$$\frac{1}{M_p}\left(\frac{\mu_0}{\mu_s}\right)\left(\frac{\mu_s}{\mu_p'}\right)\left(\frac{\mu_p'}{\mu_n}\right) = \left(\frac{1}{Nm_p}\right)\frac{\mu_0}{\mu_0(m/m_p)} = \frac{1}{Nm}.$$

The first three quantities on the left are given by Eqs. (5), (1) and (3), while on the right m may be eliminated by Eq. (2).

Thus Eqs. (6), (7) and (8) become

(17) $$h/e^2 = 2.8720818\cdot10^{-8} = B_1 \qquad (3 \text{ ppm}),$$

(18) $$e^4/Nh^3 = 3.0371164\cdot10^{17} = B_2 \qquad (7 \text{ ppm}),$$

(19) $$e^5/h^3 = 8.788366\cdot10^{31} = B_3 \qquad (15 \text{ ppm}).$$

None of the errors is significantly changed by the auxiliary constants; in the case of Eq. (17) reference to the original calculation [185] of α^{-1} will show that c appears only as $c^{-\frac{1}{2}}$ in the final result.

The solution of these equations is

(20) $$\begin{cases} e = 4.802876\cdot10^{-10} \\ h = 6.625208\cdot10^{-27} \\ N = 6.024837\cdot10^{23}. \end{cases}$$

The remaining items in Table VI will now be considered: it will first be shown that the next group, Eqs. (9), (10) and (11), should be retained. In terms of the trial data with the B's defined by Eq. (17), (18) and (19), it is seen that $F = Ne/c = B_3/(B_2c)$, with a corresponding error of $(15^2+7^2)^{\frac{1}{2}} = 17$ ppm Since the error in the electrochemical value of F given by Eq. (9) is less than twice as great, it will carry appreciable weight and should be included. With elimination of c it becomes

(21) $$Ne = 2.893420\cdot10^{14} \qquad (30 \text{ ppm}).$$

Eqs. (10) and (11) may be combined to give N with an error of 68 ppm. The trial data give

$$N = B_1^3B_2^{-1}B_3^2$$

$$\text{P.E.} = [(3\times3)^2 + 7^2 + (2\times15)^2]^{\frac{1}{2}} = 32 \text{ ppm}.$$

Since this error is only about half that obtained from Eqs. (10) and (11), they

too will be included. The resulting equation is

(22) $$N = 6.024817 \cdot 10^{23} \qquad (68 \text{ ppm}).$$

The remainder of the data, Eqs. (13) to (16), will not be used in the adjustment. As previously discussed, the GARDNER and PURCELL result Eq. (13) can also be obtained from Eqs. (1) and (3); therefore, once the theoretical relation for μ_s/μ_0 has been accepted unreservedly, Eq. (13) carries little weight.

The hyperfine structure measurement Eq. (14), determines the same quantity as the fine structure result, Eq. (6). The hfs. result carries a somewhat lower weight and differs from Eq. (6) by less than half the probable error of the latter. Therefore the practical effect of including or rejecting Eq. (13) will be small; in view of the theoretical uncertainty involved in the hfs. interpretation it seems safer to omit this item entirely.

Combining Eq. (11) with Eq. (15) gives h/e with an error of 68 ppm; combining it with Eq. (16) gives $h/(em)^{\frac{1}{2}}$ with an error of 73 ppm, The corresponding errors calculated from the direct solution data are 16 ppm and 10 ppm respectively. Hence both Eqs. (15) and (16) carry too little weight to be of value.

It should noted that the ratio λ_g/λ_s need not be treated as a variable at this stage of the adjustment since it appears in only one equation which is to be included, (Eq. (22)). Thus the data can not be correlated through this factor. After the primary constants, e, h, N, and m, have been determined, the best values of λ_g/λ_s will be considered separately.

3. – Linearized equations.

Five equations have now been selected, viz., Eqs. (17), (18), (19), (21) and (22). Mathematically these equations represent five surfaces in the three dimensional space of the variables e, h and N. If the experiments were all ideally precise, these surfaces would intersect in a common point which would then give the true values of the variables. Of course, in practice they do not quite fulfill this ideal; hence a least squares treatment becomes necessary to find the best compromise solution. However, since the surfaces all come very close to meeting in a common point, they may certainly be approximated as planes in the region of interest; in other words, the equations may be linerized.

Consider for simplicity an equation involving two variables, e and N; let $f(e, N) = e^a N^b = B$, where B is the experimentally observed value. A pair of « origin values », e_0 and N_0, which are known to be close to the final solution, may now be selected; in this analysis, the values obtained from the trial data will be used. The function $f(e, N)$ may now be expanded about this point 0 in a Taylor series, only linear terms being retained. Thus

$$f(e, N) = f(e_0, N_0) + \left(\frac{\partial f}{\partial e}\right)_0 (e - e_0) + \left(\frac{\partial f}{\partial N}\right)_0 (N - N_0) + \ldots = B\,.$$

Since $f(e, N) = e^a N^b$, the linear approximation gives

$$B - e_0^a N_0^b = (ae_0^{a-1} N_0^b)(e - e_0) + (be_0^a N_0^{b-})(N - N_0) .$$

Multiplying by $10^6/e_0^a N_0^b$ yields

$$ax_e + bx_N = \frac{B - e_0^a N_0^b}{e_0^a N_0^b} \cdot 10^6 , \tag{23}$$

where

$$x_e = \frac{e - e_0}{e_0} \cdot 10^6 , \qquad x_N = \frac{N - N_0}{N_0} \cdot 10^6 . \tag{24}$$

The x's represent differences in ppm between the values of the variables and the origin values; the term on the right gives the difference in ppm between the experimentally observed quantity and the value which would have been expected on the basis of the origin values. It will be noted that the coefficients of the x's are just the exponents of the original variables. The extension to three variables is straightforward and yields equations of the same form.

The linearized forms of the five equations to be used are given below, with the original number of the equation shown on the left. Since the direct solution values of Eq. (20) are used as origin values, the constant terms of the first three equations all vanish. Experiments are weighted inversely as the square of the probable errors; the weighting factor is $900/(\text{P.E.})^2$, where the probable error is expressed in ppm. Some of the weights have been rounded off slightly, but this is not significant in view of the uncertainty of the errors.

Original Eq.	Linearized Equations	Weight	Eq. Number
(17)	$-2x_e + x_h = 0$	100	(25)
(18)	$4x_e - 3x_h - x_N = 0$	18	(26)
(19)	$5x_e - 3x_h = 0$	4	(27)
(21)	$x_e + x_N = -81.0$	1	(28)
(22)	$x_N = -3.3$	.2	(29)

4. – Least squares solution.

The most generally accepted means of obtaining the best compromise solution for a set of overdetermined equations such as given above is the method of least squares. This is a well-known technique, which is discussed in numerous mathematical texts. (See, for example, CRAMÉR [186] or WHITTAKER and ROBINSON [187]). The application of this technique to adjustments of atomic constants has been well treated by DUMOND and COHEN [1, 29, 188]; COHEN has extended the method to the case when the experimental errors are corre-

lated. Some of the principal results needed here are summarized in Appendix B; for further details the above references should be consulted.

It should first be noted that there are no serious correlations between the above equations. Several of the equations are correlated through c, R_∞, and μ_s/μ_p; but each of these factors involves errors of about 1 ppm or less. In the case of the equation with highest weight, Eq. (25), c actually appears only as $c^{\frac{1}{2}}$ as previously noted, while μ_s/μ_p does not appear at all. Eqs. (27) and (28) are correlated by the use of the same electrical standards to determine the ampere. The error in the ampere [137] has been estimated at 6 ppm; this is about one-third the uncertainty of Eq. (27) and only one-fifth that of Eq. (28). Thus, in view of the uncertainties of the errors, it seems an unwarranted refinement to allow for the effects of these correlations.

The procedure for obtaining the normal equations is derived in Appendix B. For each variable an equation is found corresponding to minimizing the sum of the squares of the residuals with respect to that variable. This is obtained by taking the coefficient of the variable in each linear equation times the weight of the equation and multiplying through the linear equation by this factor; all of the resulting equations are then added. For example the equation corresponding to minimizing the sum with respect to x_N is obtained as follows.

$$0 - 1\cdot 18(4x_e = 3x_h - x_N - 0) + 0 + 1\cdot 1\cdot(x_e + x_N + 81.0) + 1\cdot .2(x_N + 3.3) = 0\,,$$

$$-71x_e + 54x_h + 19.2x_N + 81.66 = 0\,.$$

Equations corresponding to minimizing with respect to x_e and x_h are similarly derived. The result is

normal equations

$$\text{(30)} \qquad \begin{cases} 789x_e - 476x_h - 71x_N = -81.0\,, \\ -476x_e + 298x_h + 54x_N = 0\,, \\ -71x_e + 54x_h + 19.2x_N = -81.66\,. \end{cases}$$

The solution of the normal equations is

$$\text{(31)} \qquad \begin{cases} x_e = 13.0\,, \\ x_h = 26.1\,, \\ x_N = -29.7\,. \end{cases}$$

In terms of the original variables the solution becomes

$$\text{(32)} \qquad \begin{cases} e = 4.802\,938\cdot 10^{-10}\,, \\ h = 6.625\,381\cdot 10^{-27}\,, \\ N = 6.024\,658\cdot 10^{23}\,. \end{cases}$$

All of the figures given above are not, of course, significant in these particular variables. However, they will be retained in calculating derived quantities; the errors will then be calculated and the results appropriately rounded off.

5. – Errors.

Before the errors are computed the χ^2 test [189] will be applied to determine the consistency of the data. Clearly some such criterion is necessary to decide whether the errors have been assessed on a reasonable basis, i.e., whether the discrepancies between various experiments are of the same order as the experimental errors. The quantity χ^2 is defined by

$$\chi^2 = \sum_i \left(\frac{d_i}{\sigma_i}\right)^2 ,$$

where σ_i is the error associated with the i-th linear equation and d_i is the difference between the right and left hand sides of the i-th equation when the least squares solution values are substituted for the x's. It can be proved that the expectation value of χ^2 for N equations and n variables is $N - n$. Roughly speaking this means that if there were one variable and many experiments (equations) each term in the sum would have an average value of unity and that χ^2 would be approximately equal to N. Since n is of the same order as N, the discrepancy between the observed values and the solution values of the x's is less than that between the observed values and the true values; in fact, if $N = n$, all d_i must vanish and $\chi^2 = 0$. Hence it seems reasonable that the expected value of χ^2 is equal to the degree of overdetermination of the equations.

When the solution values of Eq. (31) are substituted back in Eq. (30), the result is

$$\chi^2 = 2.625 . \tag{33}$$

The expected value is $5 - 3 = 2$. The value actually obtained seems quite reasonable, since large statistical fluctuations are to be expected when the degree of overdetermination is so small.

The ratio of error by external consistency (based on agreement between experiments) to that by internal consistency (based on estimated errors of various experiments) is obtained by dividing χ^2 by its expected value $(N - n)$, and taking the square root, since χ^2 involves the square of the differences. Thus

$$(\text{P.E.})_{\text{ext}}/(\text{P.E.})_{\text{int}} = \sqrt{(2.625/2)} = 1.146 .$$

Hence the errors are about 15% larger by external consistency. Since this basis is thus more conservative, *all errors in the final results will be computed by external consistency.*

As shown in Appendix B, the error matrix (based on internal consistency) is simply Kg^{-1}, where K is the weighting constant (the factor 900 used in computing the weights for Eqs. (25) to (29)) and g^{-1} is the inverse of the matrix of coefficients in Eq. (30). These values must be multiplied by 1.146^2 to express the errors on the basis of external

consistency. The matrix then becomes

$$(34) \qquad (\langle \varepsilon_i \varepsilon_j \rangle) = \begin{pmatrix} e & h & N \\ 298.2 & 563.9 & -483.2 \\ 563.9 & 1074.4 & -936.4 \\ -483.2 & -936.4 & 908.3 \end{pmatrix}.$$

These terms are in (ppm)^2. The diagonal terms represent $\langle \varepsilon_i^2 \rangle$ i.e. the squares of the errors of e, h and N. Thus, for example, the probable error of h is $(1074.4)^{\frac{1}{2}} = 33$ ppm. The off-diagonal terms are needed in calculating derived quantities, as explained below.

The matrix of correlation coefficients is defined by $r_{ij} = \langle \varepsilon_i \varepsilon_j \rangle / \langle \varepsilon_i \rangle \langle \varepsilon_j \rangle$. This is easily computed to be

$$(35) \qquad (r_{ij}) = \begin{pmatrix} e & h & N \\ 1.000 & .996 & -.928 \\ .996 & 1.000 & -.948 \\ -.928 & -.948 & 1.000 \end{pmatrix}.$$

It will be noted that there is a high degree of correlation among these variables. For example, if it were found by an entirely new and more accurate experiment that the value of e should be raised, then it is almost certain that the value of h should also be raised, while the value of N should be lowered.

6. – Errors in derived quantities.

The high correlations just obtained show clearly that the errors in e, h and N can not be treated as independent in determining the errors of derived quantities. However, the correct procedure is quite simple when the error matrix has been calculated. As shown in a previous example [190], a function $f(e, N) = e^a N^b$ may be linearized in the region of interest and expressed as

$$(f - f_0)/f_0 = a x_e + b x_N .$$

If the relative errors in e and N are ε_e and ε_N respectively, then it follows that ε_f, the the resulting relative error in f, is given by

$$\varepsilon_f = a\varepsilon_e + b\varepsilon_N .$$

Hence the square of the probable error in f is given by

$$\langle \varepsilon_f^2 \rangle = \langle (a\varepsilon_e + b\varepsilon_N)^2 \rangle = a^2 \langle \varepsilon_e^2 \rangle + 2ab \langle \varepsilon_e \varepsilon_N \rangle + b^2 \langle \varepsilon_N^2 \rangle .$$

The generalization to three variables is straightforward.

As an illustration, the error in the fine structure constant $\alpha = 2\pi e^2/hc$ will be computed. The factor 2π is known exactly; since c is an auxiliary constant, its error may

be neglected. Thus the probable error of e^2/h must be computed. This is given by

$$\langle \varepsilon_\alpha^2 \rangle = 4\langle \varepsilon_e^2 \rangle + 2 \cdot 2 \cdot (-1)\langle \varepsilon_e \varepsilon_h \rangle + \langle \varepsilon_h^2 \rangle ,$$

$$\langle \varepsilon_\alpha^2 \rangle = 4 \cdot 298.2 - 4 \cdot 563.9 + 1074.4 = 11.6 .$$

The probable error in α is then $\sqrt{11.6} \approx 3.4$ ppm, which is much less than the probable error in either h or e. This result was to be expected since α is determined principally by the fine structure experiment, Eq. (25), which gave α with an error of 3 ppm.

It may be noted that the correlation coefficients in Eq. (35) can never be greater than unity. Consequently the error of a product of two factors can never be greater than the sum of the errors of the individual factors nor less than the difference. Hence correlation coefficients may have an important role only when the errors of the two factors are comparable in magnitude.

7. – Calculation of λ_g/λ_s.

It still remains to calculate λ_g/λ_s, one of the primary objects of this investigation. There are now available two ways of determining this quantity. The direct ruled grating measurement, Eq. (11), gave

(36) $$\lambda_g/\lambda_s = 1.00202 \qquad (20 \text{ ppm}).$$

On the other hand, it may also be determined from Eq. (10) together with the least squares value of N from Eq. (32). This yields

(37) $$\lambda_g/\lambda_s = 1.002029 \qquad (11 \text{ ppm for weighting})$$

where the error quoted represents *only the error* of Eq. (10) after taking the cube root. If these are weighted inversely as the square of the errors quoted, the mean is $\lambda_g/\lambda_s = 1.002027$. It may be shown that this result is exactly the same as would have been obtained by including λ_g/λ_s as one of the variables in the adjustment. Since the algebra is somewhat lengthy, the proof of this statement will be omitted.

The error can not be calculated rigorously by a simple combination of the errors in Eqs. (36) and (37). However, it is certainly less than the 20 ppm of Eq. (36), on the basis of internal consistency. By assuming for the moment that Eqs. (36) and (37) are completely independent and including the least squares error in N in Eq. (37), it follows that the error in the mean value of λ_g/λ_s is about 12 ppm. Thus the error would appear to lie betwen 10 and 20 ppm. Since most errors are to be rounded off to one significant figure, a further study seems superfluous. The result will be stated as

(38) $$\lambda_g/\lambda_s = 1.00203 \pm .00002 .$$

In the judgment of the writers the above value is the best choice on the basis of the data available. However, it differs from the accepted value [3] now in general use by about half a probable error. It does not therefore appear possible to make a strong case for any change in the accepted value.

8. – Transformation of variables.

For the purpose of plotting a consistency chart, it is convenient to make a transformation from the quantities e, h and N to new variables α', F' and β. The transformation is indicated below, both in terms of the original variables and in the linearized forms

$$(39)\qquad \begin{cases} \alpha' = e^2/h & x_{\alpha'} = 2x_e - x_h\,, \\ F' = Ne & x_{F'} = x_e + x_N\,, \\ \beta = e^5/h^3 & x_{\beta'} = 5x_e - 3x_h\,. \end{cases}$$

Eqs. (25) to (29) now transform to

$$(40)\qquad -x_{\alpha'} = 0 \qquad (3\text{ ppm})\,,$$

$$(41)\qquad -x_{F'} + x_\beta = 0 \qquad (7\text{ ppm})\,,$$

$$(42)\qquad x_\beta = 0 \qquad (15\text{ ppm})\,,$$

$$(43)\qquad x_{F'} = -81.0 \qquad (30\text{ ppm})\,,$$

$$(44)\qquad -3x_{\alpha'} + x_{F'} + x_\beta = -3.3 \qquad (68\text{ ppm})\,.$$

Combining Eqs. (40) and (44) yields

$$(45)\qquad x_{F'} + x_\beta = -3.3 \qquad (68\text{ ppm})\,.$$

Actually this transformation might have been employed earlier. α' could have been treated as an auxiliary constant since it is essentially determined by one equation, and the adjustment carried out with two variables. The final result would not have been changed by more than small fractions of the probable errors.

D) Conclusions

1. – Recommended values (with tables).

Table VII gives the values obtained for the principal constants; Table VIII lists the conversion factors for various energy units in common use. These values are recommended by the writers for general adoption.

It should be noted that nuclear masses have not been studied as critically as other data, although they are believed to be of ample accuracy for use as auxiliary constants in deriving most other results. Also the value of pV at standard conditions has been taken from chemical sources [191] and not studied in detail; this affects the value of R, k, V_0, and constants derived from them.

TABLE VII. – *Values of atomic constants as of August* 1955.

Note. – These constants are arranged alphabetically according to the usual symbols employed for them; Greek letters are included after the English equivalents. Atomic masses are all denoted by M with the proper subscripts. All atomic masses are on the physical scale.

a_0	First Bohr radius	$(5.291\,73 \pm .000\,02)\cdot 10^{-9}$ cm
α	Fine structure constant	$(7.297\,29 \pm .000\,03)\cdot 10^{-3}$
α^{-1}		$137.037\,1 \pm .000\,5$
c	Velocity of light	$(2.997\,928 \pm .000\,004)\cdot 10^{10}$ cm s^{-1}
$c_1 = 8\pi hc$	First radiation constant	$(4.992\,0 \pm .000\,2)\cdot 10^{-15}$ erg cm
$c_2 = hc/k$	Second radiation constant	$(1.438\,79 \pm .000\,03)$ cm °K
e	Electronic charge	$(4.802\,94 \pm .000\,08)\cdot 10^{-10}$ esu
e/c		$(1.602\,09 \pm .000\,03)\cdot 10^{-20}$ emu
e/m	Specific electronic charge	$(5.272\,99 \pm .000\,08)\cdot 10^{17}$ esu g^{-1}
e/mc		$(1.758\,88 \pm .000\,03)\cdot 10^{7}$ g^{-1} s cm^{-1}
F	Faraday constant	$(9\,652.0 \pm .2)$ emu eq^{-1}
γ_p	Gyromagnetic ratio of proton	$(2.675\,27 \pm .000\,06)\cdot 10^{4}$ Oe^{-1} s^{-1}
$\gamma_{p'}$	Apparent value of γ_p in oil	$(2.675\,19 \pm .000\,06)\cdot 10^{4}$ Oe^{-1} s^{-1}
h	Planck's constant	$(6.625\,4 \pm .000\,2)\cdot 10^{-27}$ erg s
$\hbar$		$(1.054\,46 \pm .000\,04)\cdot 10^{-27}$ erg s
h/e		$(1.379\,44 \pm .000\,02)\cdot 10^{-17}$ erg s esu^{-1}
h/m		$(7.273\,78 \pm .000\,05)$ cm^2 s^{-1}
k	Boltzmann's constant	$(1.380\,49 \pm .000\,05)\cdot 10^{-16}$ erg °K^{-1}
λ_{cc}	Compton wave-length of electron	$(2.426\,27 \pm .000\,02)\cdot 10^{-10}$ cm
λ_{cp}	Compton wave-length of proton	$(1.321\,40 \pm .000\,02)\cdot 10^{-13}$ cm
λ_g/λ_s	Conversion factor from Siegbahn X-ray scale to absolute units	$1.002\,03 \pm .000\,02$
$\lambda_m T$	Wien's displacement law constant	$(.289\,780 \pm .000\,005)$ cm °K

(TABLE VII *continued.*)

λ_0	Wave-length associated with 1 eV	$(1.239\,78 \pm .000\,02)\cdot 10^{-4}$ cm
M_D	Atomic mass of deuterium	$(2.014\,740 \pm .000\,002)$ amu
M_d	Atomic mass of deuteron	$(2.014\,191 \pm .000\,002)$ amu
$M_e = Nm$	Atomic mass of electron	$(5.487\,60 \pm .000\,04)\cdot 10^{-4}$ amu
M_H	Atomic mass of hydrogen	$(1.008\,144\,5 \pm .000\,001\,0)$ amu
M_{n_0}	Atomic mass of neutron	$(1.008\,984 \pm .000\,002)$ amu
M_p	Atomic mass of proton	$(1.007\,595\,7 \pm .000\,001\,0)$ amu
M_p/M_e	Ratio of proton to electron mass	$1\,836.13 \pm .02$
m	Electron mass	$(9.108\,6 \pm .000\,3)\cdot 10^{-28}$ g
m_{n_0}	Neutron mass	$(1.674\,76 \pm .000\,05)\cdot 10^{-24}$ g
m_p	Proton mass	$(1.672\,45 \pm .000\,05)\cdot 10^{-24}$ g
μ	Reduced mass of electron in H atom	$(9.103\,6 \pm .000\,3)\cdot 10^{-28}$ g
μ_n	Nuclear magneton	$(.505\,05 \pm .000\,02)\cdot 10^{-23}$ erg Oe^{-1}
μ_0	Bohr magneton	$(.927\,33_4 \pm .000\,02)\cdot 10^{-20}$ erg Oe^{-1}
μ_p	Magnetic moment of proton	$(1.410\,48 \pm .000\,03)\cdot 10^{-23}$ erg Oe^{-1}
μ_s	Magnetic moment of electron	$(.928\,40 \pm .000\,02)\cdot 10^{-20}$ erg Oe^{-1}
μ_s/μ_0		1.001 145 4 (theoretical)
μ_s/μ_p		$658.211 \pm .001$
N	Avogadro's number	$(6.024\,7 \pm .000\,2)\cdot 10^{23}$ $mole^{-1}$
$n_0 = N/V_0$	Loschmidt's number	$(2.687\,09 \pm .000\,09)\cdot 10^{19}$ cm^{-3}
p_0	Standard atmosphere	$1.013\,250\cdot 10^6$ dyn cm^{-2} (*)
R	Ideal gas constant	$(8.317\,0 \pm .000\,1)\cdot 10^7$ erg $°K^{-1}$ $mole^{-1}$
R_D	Rydberg constant for D	$109\,707.42 \pm .01$ cm^{-1}
R_H	Rydberg constant for H	$109\,677.57_6 \pm .01$ cm^{-1}
R_∞	Rydberg constant for infinite mass	$109\,737.31 \pm .01$ cm^{-1}
r	Ratio of physical to chemical scale of atomic weights	1.000 275 (*)
σ	Stefan-Boltzmann constant	$(5.669\,6 \pm .000\,4)\cdot 10^{-5}$ erg cm^{-2} s^{-1} $°K^{-4}$
V_0	Molar volume	$(2.242\,08 \pm .000\,03)\cdot 10^4$ cm^3 $mole^{-1}$

*) Conventionally adopted values.

TABLE VIII. – *Energy conversion factors.*

erg	V	s^{-1}	cm^{-1}	°K	g	amu
1 erg	$6.2419 \cdot 10^{11}$	$1.50935 \cdot 10^{26}$	$5.0346 \cdot 10^{15}$	$7.2438 \cdot 10^{15}$	$1.112648 \cdot 10^{-21}$	$6.7033 \cdot 10^{2}$
$1.60209 \cdot 10^{-12}$	1 V	$2.41810 \cdot 10^{14}$	$8.0659 \cdot 10^{3}$	$1.16052 \cdot 10^{4}$	$1.78256 \cdot 10^{-33}$	$1.07393 \cdot 10^{-9}$
$6.6254 \cdot 10^{-27}$	$4.13547 \cdot 10^{-15}$	1 s^{-1}	$3.335637 \cdot 10^{-11}$	$4.79929 \cdot 10^{-11}$	$7.3717 \cdot 10^{-48}$	$4.44121 \cdot 10^{-24}$
$1.98624 \cdot 10^{-16}$	$1.23978 \cdot 10^{-4}$	$2.997928 \cdot 10^{10}$	1 cm^{-1}	1.43879	$2.20999 \cdot 10^{-37}$	$1.33144 \cdot 10^{-13}$
$1.38049 \cdot 10^{-16}$	$8.6168 \cdot 10^{-5}$	$2.08364 \cdot 10^{10}$	.69503	1 °K	$1.53600 \cdot 10^{-37}$	$9.2538 \cdot 10^{-14}$
$8.98757 \cdot 10^{20}$	$5.6099 \cdot 10^{32}$	$1.35654 \cdot 10^{47}$	$4.5249 \cdot 10^{36}$	$6.5104 \cdot 10^{36}$	1 g	$6.0247 \cdot 10^{23}$
$1.49180 \cdot 10^{-3}$	$9.3116 \cdot 10^{8}$	$2.25164 \cdot 10^{23}$	$7.51066 \cdot 10^{12}$	$1.08063 \cdot 10^{13}$	$1.65985 \cdot 10^{-24}$	1 amu

Note. - The above table is to be read horizontally. For example, 1 erg is equal to $6.7033 \cdot 10^{2}$ amu, i.e., the conversion factor is $6.7033 \cdot 10^{2}$ amu/erg.
The probable error indicates an uncertainty in the last digit of each factor.

The value of λ_p/λ_s quoted here is slightly higher than the presently accepted value of 1.00202. However, since the difference is only about half the probable error, there is no compelling reason for discarding the present widely accepted value.

As elsewhere in this report, the errors given are probable errors; it is therefore to be expected that the true values lie outside the stated limits in some cases.

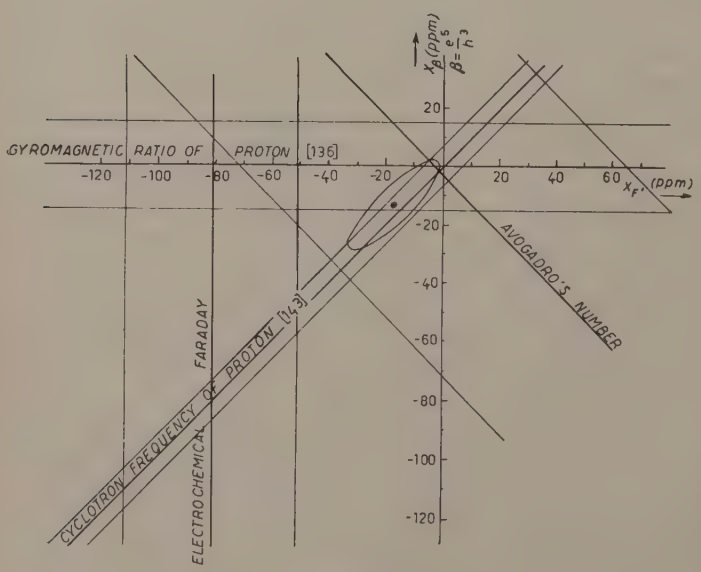


Fig. 18.

2. – Consistency of data.

In many studies of the constants an isometric consistency chart introduced by DUMOND [192] has been used to present the adjustment graphically. However, in the present instance a still simpler picture may be obtained by using the transformation of variables previously given [193]. This transformation shows

that the fine structure equation is nearly independent of the other equations and that α' may be used, without serious error, as an auxiliary constant in the one other equation where it appears. Thus the essential features of the adjustment may be shown in a two-dimensional plot using the variables $F' = Ne$ and $\beta = e^5/h^3$. This is given in Fig. 18.

Since F', is proportional to the faraday constant $F = Ne/c$, the effect of changing the electrochemical value of F may easily be seen by moving the vertical line representing this experiment to the right or left by the desired number of ppm. By a fortunate coincidence the other three equations all contain x_β to the first power. Thus the effect of changing any one of these experimental values by a given number of ppm may be seen by moving the line parallel to itself and changing its β intercept by the same number of ppm.

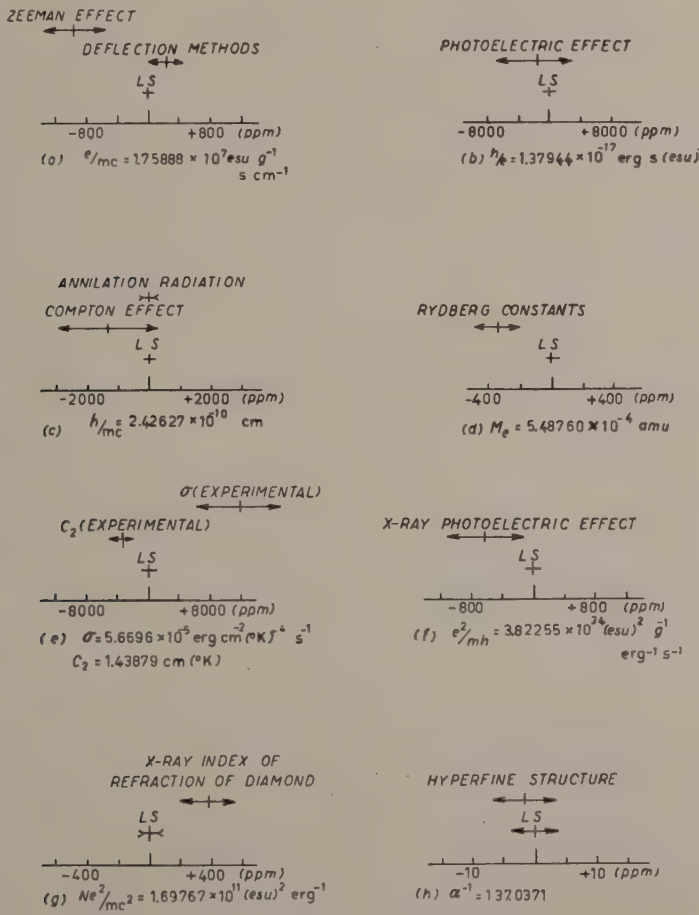


Fig. 19.

The adjusted least squares values and the ellipsoid of error are also indicated in Fig. 18. It is clear that the adjusted values are in excellent agreement with all

experiments except the electrochemical faraday and that the discrepancy is not too implausible even in this case.

The other experiments, which were not used in the adjustment, will now be considered briefly. The various graphs in Fig. 19 compare the adjusted least squares values with the less accurate data. The least squares values are denoted by « LS »; in most cases, where the corresponding errors are too small to be seen on the scale used, the LS values are simply indicated by crosses. The origin is taken as the LS result, which is the numerical value given; the deviation of other experimental values and the spread of the probable errors are then shown in terms of ppm. The oil drop determination of the electronic charge is omitted for reasons previously stated [194].

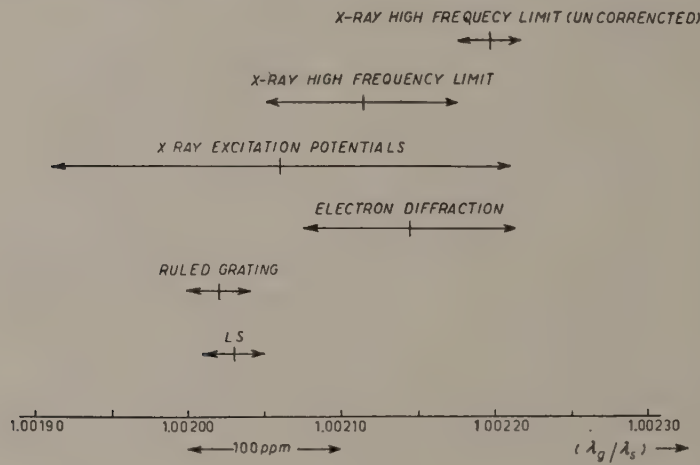


Fig. 20.

Almost half of the probable errors overlap the least squares values; in no case is the discrepancy greater than three probable errors. This may be considered as fairly satisfactory agreement. One of the worst discrepancies is in the experimental value of σ; this may come from some uncertainty in the temperature scale, as mentioned earlier [195].

Three of the X-ray results are presented in a slightly different manner in Fig. 20. Each of the experiments shown is tentatively assumed correct and used to calculate a value of λ_g/λ_s with the aid of the least squares data for the other constants. The ruled grating value as well as the least squares value of λ_g/λ_s are given for comparison. Nilsson's measurements of excitation potentials are in excellent agreement with the least squares value. The results of the electron diffraction work may be considered in fair agreement in view of its probable error. The same holds for the measurement of the X-ray high frequency limit in the corrected version adopted in the present report.

However, the corresponding uncorrected value with its original weight is seen to disagree drastically with the least squares result. It is believed that the reasons previously cited [196] account for most of the discrepancy. Use of the uncorrected figure with its original weight obviously accounts for the high values of λ_g/λ_s obtained in previous evaluations. If the reasoning of this report is valid, such a procedure must now be considered erroneous and the resulting high values of λ_g/λ_s ignored.

3. – Recommendations for new experiments.

a) The principal discrepancy in the present adjustment seems to be that between the electrochemical value of the faraday and that implied by the other experiments. The most likely causes seem to lie in the uncertainty as to the purity of the sodium oxalate used by CRAIG and HOFFMAN and the uncertainty in the isotopic abundances and therefore the atomic mass of silver. Further refinement of the CRAIG and HOFFMAN work, as well as the necessary measurements on silver would seem to be of first importance.

b) New theoretical work leading to a better interpretation of the observed isochromats in the X-ray « h/e experiments » would be highly desirable. If properly interpreted, these experiments might again play an important part in fixing the atomic constants.

c) There is still some evidence for a possible variation in the velocity of light with frequency, although the negative case appears much stronger. One more optical measurement confirming Bergstrand's value would do much to settle any lingering doubts. In this connection, the possibility of refining Houston's method deserves study.

d) In view of the very limited amount of overdetermination in the present adjustment, any new precision experiments (with errors of the orders of 10 ppm) would be of great value. For example, SIEGBAHN's [197] proposed method of measuring h/e by β-ray spectroscopy warrants careful consideration.

In the final analysis, improvement in our knowledge of the atomic constants depends primarily on new and more accurate experiments. If this report serves in any way to clarify the present situation and to encourage new work along useful lines, it has fulfilled a major purpose.

* * *

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It is probably impossible at the present time to compile a complete list of those who have contributed significantly to this work. However, the writers are particularly indebted to the following workers: Drs. J. I. HOFFMAN and

D. N. CRAIG for several valuable discussions on the electrochemical measurement of the Faraday; Dr. J. A. HIPPLE for detailed discussion of the measurements of the gyromagnetic ratio of the proton and the cyclotron frequency of the proton, as well as the problem of the best value of the Faraday; Mr. R. DRISCOLL for informative conversations on the absolute determination of the ampere and for reviewing some of the work on the gyromagnetic ratio of the proton to answer questions raised by the authors; Dr. J. L. THOMAS for recalibrating certain electrical standards in a search for the possible cause of the h/e discrepancy; Dr. D. H. RANK for a full discussion of his measurement of c before publication; Dr. E. S. DAYHOFF for many informative conversations on the fine structure measurement and the determination of c; Dr. H. M. WATTS for his assistance in many ways during the early part of the study; Dr. E. E. SALPETER for valuable advice on the interpretation of the fine structure and hyperfine structure measurements; Dr. H. LYON for helpful discussions of the velocity of light; and Dr. T. H. BERLIN for reviewing and criticizing the section on quantum electrodynamic experiments as well as his assistance in other matters.

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APPENDIX A

Recent developments

1. – Velocity of light.

SILSBEE and GARDNER [198] have recalculated the results of the Rosa and Dorsey experiment, correcting it for humidity of the air and for the best conversion factors between the old international electrical units and absolute

units. They obtained (299 800 ± 31) km/s; this would raise the old Birge average by about 1 km/s. RANK [199] has recently revised his value of c as a result of a more precise determination of the band origin used in his infra-red work; his new figure is (299 791.9 ± 2.2) km/s. HOUSTOUN [200] has recalculated his result, using a more precise correction for the refractive index of air, and obtained 299 782 km/s. All of these revisions bring the respective experiments in better agreement with the value recommended in the present report.

HENDERSON and MUNGALL [201] have reported a resonant cavity measurement at 400 MHz, which gave $c = 299\,780$ km/s. However, they concluded that various systematic errors were sufficient to explain the discrepancy between their result and the accepted value.

Three new precision measurements [202] of c have been carried out with the Bergstrand geodimeter, in Sweden, Great Britain, and Australia respectively. All of the results were about .8 km/s lower than Bergstrand's. Although these results could conceivably all have some systematic errors in common with Bergstrand, it is difficult to imagine a significant one which would be essentially independent of length of base line. Furthermore, in the case of the British measurement the frequency of the crystal was independently calibrated.

While in the opinion of the authors it would still be desirable to have another completely independent precision measurement at an optical frequency, preferably in vacuum, the need for such confirmation has certainly lessened. As for the recommended value, the lowering of the geodimeter value is partially compensated by the rise in Rank's result; the weighted mean is not changed significantly.

2. – Avogadro's number (X-ray crystal density method).

SMAKULA, KALNAJS and SILS [203] have completed a series of measurements of crystal densities and lattice spacings (by X-ray measurements). The best results were obtained with Si, Al, CaF_2 and Ge; these gave values of Avogadro's number mutually agreeing within 10 ppm, with the average value of N' about 80 ppm higher than the calcite figure used by the authors. (An error in the calculated calcite value might be explained if the impurity atoms occur interstitially rather than substitutionally, as assumed in the Birge and Brogren corrections). If the accuracy is as high as indicated by the excellent internal agreement for different crystals, this average should probably be adopted to the exclusion of calcite data. The only effect of major significance would be on λ_p/λ_s. The value implied by N' would then be 1.002 05 and the weighted average about 1.002 04.

However, there are possible sources of systematic errors common to all these measurements, both in the X-ray spectrometer and in the density measurements. (For instance, the density of quartz was determined as an intermediate step in the weighing; this density was in serious disagreement with some of the previous measurements, e.g., DuMond's). Thus it seems premature to put the entire weight on these values. In any event, the change in λ_p/λ_s would only be about half its assigned probable error.

3. – Mass of the proton.

QUISENBERRY, SCOLMAN and NIER [204] have performed a new and highly precise measurement of the mass of the proton, obtaining $M_H = (1.0081442 \pm \pm .0000002)$ amu. A new evaluation of nuclear data by WAPSTRA [205] leads to a value $M_H = 1.0081452$ amu. Both results fall within the probable error of the value recommended here.

4. – X-Ray « h/e experiments ».

KERSCHER and KULENKAMPFF [206] and SCHEER and ZEITLER [207] have made experimental and theoretical studies respectively of thin-target X-ray spectra; however, they are concerned primarily with angular distribution. ALBERT [208] has carried out further work on the correlation between discrete electron losses and the form of the X-ray isochromat near cut-off frequency; his theory now includes a qualitative explanation of the observed minima. Recent developments in measurement of discrete electron losses and their correlation with X-ray fine structure has been well summarized by LEDER, MENDLOWITZ and MARTON [209]. While all of this new work seems to strengthen the analysis of the X-ray « h/e experiments » presented in this report, it would not appear that it is yet possible to interpret the results of these experiments with any higher accuracy.

5. – Gyromagnetic ratio of the proton.

The gyromagnetic ratio of the proton has been measured by KIRCHNER and WILHELMY [210] in a new experiment employing an iron-free field, who obtained a value $\gamma_p' = 2.67562 \pm .00016$. This figure is about 150 ppm higher than that of THOMAS, DRISCOLL and HIPPLE, the difference being considerably greater than the sum of the errors. They suggest that the difference may be due to a discrepancy in electrical conversion factors and plan to continue their work. Meanwhile at the Bureau of Standards in Washington work is well under way on a new and more precise determination, also using an iron-free field.

6. – Cyclotron resonance frequency of the proton.

TRIGGER [211] has refined the Jeffries experiment with the inverted cyclotron. The effect of impurities and of stray electric and magnetic fields was carefully investigated. Furthermore he developed a more exact theory of the operation of the cyclotron, including certain non-linear terms in his equations and solving them with the aid of an IBM computer. The preliminary result indicates $\mu_p'/\mu_n = 2.79267 \pm .00010$, without diamagnetic correction. Still more refined calculations are in progress. His work essentially answers the criticism of the Jeffries value advanced in this report.

Another precise measurement of the same quantity has been reported by COLLINGTON, DELLIS, SANDERS and TUBERFIELD [212]. They employed a modified form of inverted cyclotron with two grounded outer dees and a straight center conductor connected to a high frequency source. This was designed so that at resonance all protons approached asymptotically a particular circular orbit, in which the transit time between the dees was exactly one cycle of the rf. source. They obtained $\mu_p'/\mu_n = 2.792\,73 \pm .000\,04$, without diamagnetic correction; the error is intended as a limit of error.

Both of these results are essentially in agreement with the Sommer, Thomas and Hipple value used in the present study. A properly weighted average might now give about 2.792 70; in view of the external consistency of the data the present error could not be appreciably decreased. The effect on most of the other constants would be very small and, in consideration of the proisional character of the Trigger value, there seems as yet no reason for a change.

7. – Hyperfine structure of hydrogen.

The hyperfine splitting of H has been remeasured with improved apparatus by KUSCH [213], who now reports $\Delta\nu(\mathrm{H}) = (1\,420.405\,73 \pm .000\,05)$ MHz, in essential agreement with the result of Dicke. However, the theoretical interpretation of the hfs. still appears unsatisfactory. More precise calculations of the «average excitation potential» have been carried out by HARRIMAN [214]. MOELLERING, ZEMACH, KLEIN and LOW [215] have used the hfs. result to estimate the spatial extent of the proton magnetic moment; this i just the reverse of the procedure which would be desirable from the standpoint of evaluation of atomic constants.

HEBERLE, REICH and KUSCH [216] have determined the hfs. splitting in the metastable $2S$ state; the ratio $\Delta\nu(2S)/\Delta\nu(1S)$ checks with present theoretical predictions within about 1 ppm. However, it would appear that this new datum has the same uncertainty in interpretation as for the $1S$ state, in so far as the calculation of the fine structure constant α is concerned.

More precise theoretical knowledge would be of great value since without it the highly weighted fine structure determination of α stands virtually alone, without any other data of comparable accuracy to confirm or disprove it. Of course, new microwave fine-structure measurements might serve the same purpose.

8. – β-Ray spectroscopic measurements.

SIEGBAHN and EDVARSON [217] have recently reported a value of $(h/mc) = (2.426\,2 \pm .001\,6) \cdot 10^{-10}$ cm, obtained by β-ray spectroscopy on electrons ejected by internal conversion of β-rays. When a number of lines are measured and the energy differences of various initial electronic states known from X-ray data, the necessary relativistic equations can be solved for h/mc. In this procedure errors are compounded in such a way that the accuracy is low; while the individual lines are measured to about 10 ppm, the above error is given

as almost 700 ppm. Thus it can not as yet carry significant weight in evaluating atomic constants. However, it is in almost perfect agreement with the values recommended here. It may also be noted that SIEGBAHN [197] has proposed a rather similar method for determining h/e.

9. – Other evaluations and reviews.

STILLE [218] has carried out studies of various atomic constants, leading to recommended values for c, F, e, N and k. Within their errors, these values agree with those recommended here; but the errors are much higher. More recently he has published a book [219] on physical units and constants, but the writers have not yet had an opportunity to study this work. Mention should also be made of a review of the velocity of light by A. KAROLUS [220].

Almost simultaneously with the completion of the body of the present report, in August 1955, COHEN, DUMOND, LAYTON and ROLLETT [221] published a new adjustment of the atomic constants. This was primarily based on data which they used in their 1952 evaluation, but involved a systematic analysis of variance in an effort to eliminate experiments with unsuspected systematic errors. It was reassuring to find that their conclusions in regard to the X-ray « h/e experiments » were substantially the same as reached by the writers. They further pointed out that in order to make all three « h/e experiments » agree satisfactorily the form of the ideal isochromat must be assumed to be voltage dependent, a point not properly emphasized by the present authors. On the other hand, even after offering a tentative explanation of the systematic error, they retained the least accurate of these three experiments in the final evaluation. Although the practical effect of this is small, it certainly appears more logical to reject all three of the questionable items. (Thus the adjustment denoted as 1111120 in Table IV of their paper would appear to be the best choice. After allowing for the fact that it has one less degree of freedom than the one they adopt, the value of χ^2 is still considerably more favorable).

They also differed from the present analysis in the use of electrochemical data. They used only silver and iodine values, with the latter based on an older value of atomic mass; furthermore the errors quoted for these measurements appear very low. As a result, they retained the iodine value, which is in almost perfect agreement with electromagnetic experiments, and rejected the silver one. (The writers considered the same thing during the early stages of their work). However, with the iodine result revised for the latest value of atomic mass and the Craig and Hoffman figure included, there are three electrochemical values in fair agreement with one another, all lower than the electromagnetic value. Hence it now appears very questionable to completely reject the silver result. As a result, the CDLR [221] value of faraday differs from that recommended here by almost three times the probable error of the former; there are lesser effects on the values of other constants.

Finally they employed Birge's average for the measurement of Avogadro's number by means of the X-ray crystal density method; this gives a figure for N' about 60 ppm higher than the revised calcite value used by the writers. However, as noted earlier in this Appendix, the SMAKULA, KALNAJS and SILS

data indicates that the Birge average should be raised rather than lowered. Thus the CDLR evaluation seems to occupy a safe middle ground in this respect. At any rate the practical effect of this difference is small, except perhaps on the recommended value of λ_o/λ_s.

COHEN [222] recently developed a more precise method for evaluating the significance of differences between items of input data and least-squares output values. He concluded that none of the items retained in the CDLR study (except possibly the BEARDEN and SCHWARZ « h/e experiment ») showed significant differences.

APPENDIX B

Summary of the theory of least squares

1. – Most probable values of the variables.

Consider a set of N *experiments* to determine n *variables*, where $N > n$. Assume that all of the experimental equations can be linearized as described in Sect. *C*. 3. Then the i-th experiment is described by the equation

$$\sum_{r=1}^{n} a_{ir} x_r = c_i \,. \qquad 1 \leqslant i \leqslant N. \tag{B.1}$$

The matrix a is thus a rectangular (N row $\times n$ column) matrix. Assume further that the experiments are completely independent (no correlation of errors) and that the errors have a Gaussian distribution. Let σ_i be the standard deviation of the i-th equation.

Since the set of equations is overdetermined, it will in general be impossible to find a set of x's which satisfy all equations simultaneously. Let r_i be the difference between the right and left sides of Eq. (B.1) for a given set of x's. On the basis of the i-th experiment the probability of these values being correct is proportional to

$$\exp\left[-r_i^2/2\sigma_i^2\right] .$$

Since the experimental errors are all independent, then on the basis of all the experiments the probability of a given set of x's being the correct one is simply proportional to a product of N such factors, viz.,

$$\exp\left[-\tfrac{1}{2}\sum_{i=1}^{N}\frac{r_i^2}{\sigma_i^2}\right] .$$

To find the best compromise value (the most likely value) the above probability must be maximized, i.e. the sum must be minimized; hence the name

« least squares » is used. In terms of the x's this sum becomes

$$\sum_{i=1}^{N} \frac{r_i^2}{\sigma_i^2} = \sum_{i=1}^{N} \left(\frac{1}{\sigma_i^2}\right) \left(\sum_{r=1}^{n} a_{ir}x_r - c_i\right)^2 . \tag{B.2}$$

The factor $(1/\sigma_i^2)$ may equally well be taken as K/σ_i^2, where K is any convenient constant; this will not affect the values of the x's which give a minimum.

To minimize the sum it must be differentiated with respect to each x in turn and each derivative set equal to zero. The p-th equation obtained in this manner is

$$\sum_{i=1}^{N} \left(\frac{K}{\sigma_i^2}\right) a_{ip} \left(\sum_{r=1}^{n} a_{ir}x_r - c_i\right) = 0 . \qquad 1 \leqslant p \leqslant n. \tag{B.3}$$

There are n such equations known as « normal equations »; these uniquely determine the best values of the x's. The normal equations may be put in the form

$$\sum_{r=1}^{n} g_{pr}x_r = h_p , \tag{B.4}$$

where

$$g_{pr} = \sum_{i=1}^{N} \left(\frac{K}{\sigma_i^2}\right) a_{ip}a_{ir} , \qquad h_p = \sum_{i=1}^{N} \left(\frac{K}{\sigma_i^2}\right) a_{ip}c_i . \tag{B.5}$$

It is clear that the matrix g is a square symmetric $n \times n$ matrix. The solution is

$$x_r = \sum_{p=1}^{n} g_{rp}^{-1}h_p , \tag{B.6}$$

where g_{rp}^{-1} is the rp-th element of the reciprocal of the matrix g.

2. – Probable errors of the variables.

Let ε_r be the error associated with the calculated value of x_i: Since ε_r is equally likely to be positive or negative, its average value is zero. However, $\langle \varepsilon_r^2 \rangle$, the average value of the square of ε_r, is non-zero and will now be computed. As the average of the product of errors, $\langle \varepsilon_r \varepsilon_t \rangle$ will also be needed, it will be calculated at the outset; $\langle \varepsilon_r^2 \rangle$ may then be obtained as a special case by putting $r = t$.

In the following analysis, i and j will be used for indices ranging from 1 to N (number of experiments), while p, r, s and t will denote indices ranging from 1 to n (number of variables). Combining Eqs. (B.6) and (B.5) gives

$$x_r = \sum_{p=1}^{n} g_{rp}^{-1}h_p = \sum_{p=1}^{n} g_{rp}^{-1} \sum_{i=1}^{N} \left(\frac{K}{\sigma_i^2}\right) a_{ip}c_i . \tag{B.7}$$

Each constant c_i is, of course, equal to its true value plus some error δ_i. The corresponding error in x_r is

$$\varepsilon_r = \sum_{p=1}^{n} g_{rp}^{-1} \sum_{i=1}^{N} \left(\frac{K}{\sigma_i^2}\right) a_{ip}\delta_i \,. \tag{B.8}$$

Hence

$$\varepsilon_r\varepsilon_t = \left[\sum_{p=1}^{n} g_{rp}^{-1} \sum_{i=1}^{N} \left(\frac{K}{\sigma_i^2}\right) a_{ip}\delta_i\right]\left[\sum_{s=1}^{n} g_{ts}^{-1} \sum_{j=1}^{N} \left(\frac{K}{\sigma_j^2}\right) a_{js}\delta_j\right]. \tag{B.9}$$

Since all factors on the right are known constants except δ_i and δ_j, the average value is given by

$$\langle\varepsilon_r\varepsilon_t\rangle = \sum_{p=1}^{n}\sum_{s=1}^{n} g_{rp}^{-1} g_{ts}^{-1} \sum_{i=1}^{N}\sum_{j=1}^{N} \left(\frac{K}{\sigma_i^2}\right)\left(\frac{K}{\sigma_j^2}\right) a_{ip}a_{js}\langle\delta_i\delta_j\rangle \,. \tag{B.10}$$

As the experiments are assumed completely independent, their errors are uncorrelated. Therefore $\langle\delta_i\delta_j\rangle = \delta_{ij}\sigma_i^2$ where δ_{ij} is the Kronecker δ. Thus

$$\langle\varepsilon_r\varepsilon_t\rangle = \sum_{p=1}^{n}\sum_{s=1}^{n} g_{rp}^{-1} g_{ts}^{-1} \sum_{i=1}^{N} K\left(\frac{K}{\sigma_i^2}\right) a_{ip}a_{is} \,. \tag{B.11}$$

From the definition of g in Eq. (B.5) it follows that the last sum is equal to Kg_{sp}. Therefore

$$\langle\varepsilon_r\varepsilon_t\rangle = K\sum_{p=1}^{n}\sum_{s=1}^{n} g_{rp}^{-1} g_{ts}^{-1} g_{sp} \,. \tag{B.12}$$

Since $\sum_{s=1}^{n} g_{ts}^{-1} g_{sp} = \delta_{tp}$, the Kronecker δ, it follows that

$$\langle\varepsilon_r\varepsilon_t\rangle = Kg_{rt}^{-1} \,. \tag{B.13}$$

Thus $\langle\varepsilon_r^2\rangle = Kg_{rr}^{-1}$. Since the probable error is simply a constant times the standard deviation, this same method will give probable error if the experiments are weighted as $K/(\text{P.E.})^2$ instead of K/σ^2.

It must be emphasized that the above errors have been computed by internal consistency, i.e., on the basis of the errors estimated for each experiment. It may now be asked whether or not the agreement between different experiments is consistent with these estimates. This question is answered by the χ^2 test.

3. – The χ^2 test.

The χ^2 test involves the expected value of the sum in Eq. (B.2) *when the least square solution for the* x*'s is substituted in it*; in other words, it is the value of this sum after it has been minimized. If $N \gg n$, the least squares solution should approximate the true values of the variables; each term would then have an average value of unity and the sum would be approximately N. However, the case when N and n are comparable is of great practical interest.

Let d_i be the value of r_i *when the least squares solution is substituted for the* x's. Let δ_i now denote the error in c_i, which is, of course, unknown, while X_i denotes the true value of x_i, also unknown. Then, since the true value of the constant is the observed c_i minus the error δ_i, it follows that

$$\text{(B.14)} \qquad \begin{cases} \sum_{r=1}^{n} a_{ir}x_r - c_i = d_i\,, \\ \sum_{r=1}^{n} a_{ir}X_r - c_i = -\delta_i\,, \end{cases}$$

$$\text{(B.15)} \qquad \sum_{r=1}^{n} a_{ir}(x_r - X_r) = d_i + \delta_i\,.$$

The quantity $x_r - X_r$ is simply the error in x_r, i.e., ε_r.

$$\text{(B.16)} \qquad \therefore\ -d_i = \delta_i - \sum_{r=1}^{n} a_{ir}\varepsilon_r\,.$$

The expected value of χ^2 now becomes

$$\text{(B.17)} \qquad \langle\chi^2\rangle = \left\langle \sum_{i=1}^{N} \frac{d_i^2}{\sigma_i^2} \right\rangle = \left\langle \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(\delta_i - \sum_{r=1}^{n} a_{ir}\varepsilon_r)^2 \right\rangle,$$

$$\text{(B.18)} \qquad \langle\chi^2\rangle = \left\langle \sum_{i=1}^{N} \frac{\delta_i^2}{\sigma_i^2} \right\rangle - 2\left\langle \sum_{i=1}^{N}\sum_{r=1}^{n} \frac{a_{ir}\delta_i\varepsilon_r}{\sigma_i^2} \right\rangle + \left\langle \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \sum_{r=1}^{n} a_{ir}\varepsilon_r \sum_{t=1}^{n} a_{it}\varepsilon_t \right\rangle.$$

These terms will now be considered separately. Since the average value of $\langle\delta_i^2\rangle$ is σ_i^2, it follows that the first term is

$$\text{(B.19)} \qquad \left\langle \sum_{i=1}^{N} \frac{\delta_i^2}{\sigma_i^2} \right\rangle = \sum_{i=1}^{N} \frac{\langle\delta_i^2\rangle}{\sigma_i^2} = \sum_{i=1}^{N} \frac{\sigma_i^2}{\sigma_i^2} = N\,.$$

The second term may be simplified by use of Eq. (B.8) and by recalling that $\langle\delta_i\delta_j\rangle = \delta_{ij}\sigma_i^2$ (where δ_{ij} is the Kronecker δ) since the errors are independent.

$$\text{(B.20)} \qquad \left\langle \sum_{i=1}^{N}\sum_{r=1}^{n} \frac{a_{ir}\delta_i\varepsilon_r}{\sigma_i^2} \right\rangle = \left\langle \sum_{i=1}^{N}\sum_{r=1}^{n} \frac{a_{ir}\delta_i}{\sigma_i^2} \sum_{p=1}^{n} g_{rp}^{-1} \sum_{j=1}^{N} \left(\frac{K}{\sigma_j^2}\right) a_{jp}\delta_j \right\rangle =$$

$$= \sum_{r=1}^{n}\sum_{p=1}^{n} g_{rp}^{-1} \sum_{j=1}^{N}\sum_{i=1}^{N} \left(\frac{K}{\sigma_j^2}\right) \frac{a_{ir}a_{jp}}{\sigma_i^2} \langle\delta_i\delta_j\rangle = \sum_{r=1}^{n}\sum_{p=1}^{j} g_{rp}^{-1} \sum_{i=1}^{N} \left(\frac{K}{\sigma_i^2}\right) a_{ir}a_{ip}\,.$$

By Eq. (B.5) the last sum is simply g_{pr}. Hence,

$$\text{(B.21)} \qquad \left\langle \sum_{i=1}^{N}\sum_{r=1}^{n} \frac{a_{ir}\delta_i\varepsilon_r}{\sigma_i^2} \right\rangle = \sum_{r=1}^{n}\sum_{p=1}^{n} g_{rp}^{-1}g_{pr} = \sum_{r=1}^{n} \delta_{rr} = n\,.$$

The final term in the sum may be evaluated with the help of Eqs. (B.13) and (B.5)

$$\text{(B.22)} \qquad \left\langle \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \sum_{r=1}^{n} a_{ir}\varepsilon_r \sum_{t=1}^{n} a_{it}\varepsilon_t \right\rangle = \sum_{r=1}^{n}\sum_{t=1}^{n} \langle \varepsilon_r \varepsilon_t \rangle \sum_{i=1}^{N} \frac{a_{ir}a_{it}}{\sigma_i^2} = \sum_{r=1}^{n}\sum_{t=1}^{n} K g_{rt}^{-1} \left(\frac{g_{tr}}{K}\right),$$

$$\text{(B.23)} \qquad \left\langle \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \sum_{r=1}^{n} a_{ir}\varepsilon_r \sum_{t=1}^{n} a_{it}\varepsilon_t \right\rangle = \sum_{r=1}^{n} \delta_{rr} = n\,.$$

Eqs. (B.19), (B.21) and (B.23) are now substituted in Eq. (B.18) to give

$$\text{(B.24)} \qquad \langle \chi^2 \rangle = N - 2n + n = N - n\,.$$

This is the desired result. If in a given case $\chi^2 \gg N - n$, it indicates that some or all of the experimental errors have been seriously underestimated; conversely, if $\chi^2 \ll N - n$, some or all of the errors have been stated much too conservatively.

It should be noted that standard deviations, not probable errors are used in the definition of χ^2. If probable errors are used elsewhere, the sum may be taken on the basis of probable errors and then multiplied by $(.6745)^2$.

4. – Transformation and elimination of variables.

The sum in Eq. (B.2) to be minimized is a function defined in n-dimensional space. If the function is expressed in terms of different coordinates, say y's, this can not affect the geometrical point at which the function reaches its minimum. Hence it may be first expressed in terms of the y's and then minimized; when the corresponding x's are calculated from the solution in the y's, the result must be the same as if the entire problem had been solved in terms of the x's. Thus it is only a question of convenience as to what quantities are taken as the independent variables.

When one equation has a weight very much higher than the others (e.g. the equation for R_∞), it may be considered as an exact relationship defining one variable in terms of the others, i.e. reducing the number of independent variables by one. Since the final result is independent of a transformation of variables, it is a matter of indifference which variable is eliminated by this relation.

5. – Non-Gaussian error distributions.

In the case when the error distributions are not Gaussian (a most important practical case), COHEN [188] has shown that the least squares method can be derived by the Axiom of Minimum Error, i.e., the condition that the error should be a minimum with respect to possible variation of free parameters.

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